

STATIC AND DYNAMICAL EFFECTS
OF CORE HOLES
IN KLV AUGER, SXE, AND SXA SPECTRA
OF SIMPLE METALS

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Abstract

We examine the effect of the core hole on several spectroscopies used to explore the conduction band of simple metals. We show that the static effect on the valence electrons is very strong and discuss under what circumstances this effect may be seen experimentally. In KLV Auger spectra a core hole is present in both initial and final states. Thus there will be almost no dynamical effect, but the static effect must be accounted for in any quantitative calculation. We here present a full effective one-particle calculation for the KL_1V and $KL_{2,3}V$ spectra of sodium, that for the first time explain the "mystery" structure seen in experiment, by attributing this effect to the presence of a core hole. The agreement with experiment is gratifying although some discrepancy remains. For the main band of soft x-ray emission spectra the core hole is present in the initial state but not in the final state, yet the experimental spectra do not show the strong effect found in KLV. This is explained in terms

of the Final State Rule, according to which rather accurate spectra can be obtained from a one-particle calculation provided final state wave functions are used in the transition matrix elements. The dynamical switching of the core-hole potential causes a singular behavior of the x-ray edge, which according to the Final State Rule can be accounted for by multiplicative power-law factors. For the satellite emission band there is an additional core hole in both initial and final states, and, by the Final State Rule, the spectrum should show the static effect of precisely one core hole. This is confirmed by the good agreement between theory and experiment that we obtain for the $L_{2,3}$ SXE satellite spectrum of sodium. The Final State Rule is also used to explain the similar shapes of the main band and the satellite in the case of Li K emission, and for the interpretation of alloy spectra.

1. Introduction.

Several experimental techniques have been employed over the years to probe the valence bands in solids. But even in the case of simple metals, whose bandstructure is believed to be well known theoretically, the differing experimental spectra have long defied theoretical interpretation. As the same experimental methods are used to study far more complex systems as e.g. alloys in order to explore their electronic structure, it is most important that one know in detail what information on the valence bands may be inferred from a particular experiment.

In this paper we will be concerned with core-core-valence Auger electron spectra (CCV-AES) and their relation to soft x-ray emission (SXE) and absorption (SXA) spectra in simple metals, with particular emphasis on sodium. In all these spectroscopies one expects to map out the valence band directly, in contrast to e.g. CVV Auger spectra, which in the simplest approximation are related to a self-convolution of the density of states. Furthermore, since the above methods all involve one or more core holes, we also expect this map of the valence band to reflect the local electronic structure near a given site, in contrast to e.g. valence x-ray (XPS) or ultra violet (UPS) photoemission spectroscopy. As will be shown, the electronic structure is locally strongly

affected by a core hole, and for a consistent interpretation of the differing spectra not only the respective transition matrix elements but also this core hole effect needs to be considered.

KLV spectra of the simple metals sodium, magnesium, and aluminium have been reported by several workers, e.g. Fuggle et al.¹, Barrie and Street², and recently Lässer and Fuggle³. In the KLV process a hole in the K-shell (1s-shell) is filled by an electron from the L-shell (2s or 2p-shell), and the rather large energy (~ 1 keV) released in this transition is transferred to a valence electron which may leave the solid. In a one-particle picture the kinetic energy of the escaping electron is directly related to the energy of the valence state from which the Auger electron was ejected. The Auger spectrum, i.e. the plot of the number of escaping electrons per kinetic energy interval, should thus be closely related to the occupied part of the valence bands. It was therefore rather surprising when the Auger spectra turned out to have a shape quite different from both the main band of the $L_{2,3}$ emission spectrum and from the valence XPS spectrum. These latter spectra both involve a dipole matrix element. Their overall shapes reflect the occupied part of the valence band and are rather similar if we overlook the edge singularity seen in SXE. Due to dipole selection rules, the $L_{2,3}$ emission spectra give a picture of the local partial density of states of s and d character (d is almost negligible for simple metals) and, according to the Final State Rule^{4, 5}, the relevant state

density for the main band is that obtained from band theory, i.e. without taking the $L_{2,3}$ hole into account. In XPS neither the valence electron nor the photoelectron has a definite angular momentum character and the spectrum is given by some complicated average of the different angular momentum components of the valence density of states. For the simple metals both XPS⁶ and $L_{2,3}$ main band emission⁷⁻¹⁶ yield a rather structureless spectrum, whose width is determined by the occupied band width. In contrast the KL_1V ($1s - 2s$) and the $KL_{2,3}V$ ($1s - 2p$) spectra both show marked structure towards the bottom of the valence band. Up to now theoretical efforts to explain this structure have failed. In the Auger process the dipole matrix element is replaced by a Coulomb matrix element, and an explanation of these "mystery peaks" could possibly be sought in a rapid variation of this matrix element over the band. This possibility was, however, ruled out by Feibelman and McGuire¹⁷, who calculated the KLV Auger intensity using a single orthogonalized plane wave for the valence band wave function and a free atom Coulombic wave function for the outgoing Auger electron. As expected, for both KL_1V and $KL_{2,3}V$ they found broad featureless spectra very much resembling the XPS spectrum. There was no trace of the structure seen in experiment.

In retrospect the explanation for the mystery peaks seems rather obvious. Both initial and final states of the KLV Auger process have one core hole, although, being in different shells, they may affect the system somewhat differently. As mentioned above, we now know⁵ that the

local density of states (DOS) of the valence electrons is strongly distorted in the vicinity of the core hole. This effect is most pronounced for valence electrons of s character. Their smooth, almost parabolic local DOS is distorted by the core hole to exhibit a strong peak near the bottom of the band. The p electrons, on the other hand, suffer an almost uniform enhancement of their local partial DOS, hardly affecting its shape. The fact that the initial and final state core holes are different has been shown to have a negligible effect on the local DOS (cf. the equivalent core approximation¹⁸). Thus the Auger transition can be pictured as an excitation of a valence electron from an impurity site in a solid, where the required energy is supplied by an intra-core transition occurring simultaneously with the excitation process. From a many-body point of view, the satellite structure seen in the distribution of emitted electrons should therefore be rather similar to what is seen in a valence XPS experiment, and this is indeed the case³. The difference in transition matrix element between AES and valence XPS is masked by the strong distortions due to the fact that the Auger electron originates from an impurity site with a core hole. As far as the main band of the KLV Auger spectrum is concerned, the closest experimental analogy is therefore $L_{2,3}$ satellite emission. Here one monitors the energy distribution of photons emitted in a process where a valence electron drops down to fill one of two holes initially created in the 2p-shell. According to the Final State Rule⁵, this experiment will also give a picture of the local DOS of the occupied part of the valence band in

the presence of a core hole. Differences in the spectral shapes should then only reflect differences in the matrix elements. As a matter of fact, the $L_{2,3}$ satellite band in sodium is almost identical to the KL_1V Auger spectrum, which strongly supports the view presented above. The $KL_{2,3}V$ spectrum has a somewhat different shape, which is due to the fact that the matrix element involving a 2p core hole in the final state gives a different weighting of the contributions from valence electrons of s and p character. Common to all three spectra is, however, the marked structure near the bottom of the band caused by the strong distortion of the local partial DOS of s-character, which in turn is due to the presence of the core hole.

In the present paper we have recalculated the KL_V Auger intensities in sodium from an effective one-particle theory in which all one-particle states appearing in the Coulomb matrix element are obtained in the full potential of the solid including the potential from a self-consistently screened 2p-core hole. We have chosen to treat the outgoing Auger electron as a free electron outside the central cell, i.e. its wave function was taken to be an augmented spherical wave. This should, however, be an adequate approximation considering the high kinetic energy of the Auger electron ($\sim 1\text{keV}$). In Sec. 2 we describe the simplifications arising from this approximation in deriving the Auger intensity from the Golden Rule with initial and final states approximated by Slater determinants. In Sec. 3 we describe how repeated cluster calculations were used to obtain the self-

consistently screened core-hole potential and the corresponding one-particle wave functions. The good agreement that we obtain in this way with the measured Auger spectra becomes evident in Sec. 4, which also contains a discussion of the different mechanisms broadening the spectra. This agreement strongly supports the picture outlined above, which thus represents the first reliable interpretation of these spectra. It should be noted that preliminary results from this work have been published previously^{3, 19, 20}. Unfortunately an error in the Clebsh-Gordon algebra rendered the agreement with experiment less satisfactory at the time. The main message, however, remains, attributing the "mystery" structure seen in KLV spectra to the core hole perturbing the valence electrons. In Sec. 5 we use the Final State Rule^{4, 5} and the impurity wave functions from Sec. 3 to calculate the $L_{2,3}$ satellite emission band. Again the strong effect of the core hole is obvious and the agreement with the measured satellite band is very gratifying. We also compare the satellite band to the main band which according to the Final State Rule should not show any influence of the core hole. Experiment again agrees well with our calculated main band obtained from wave functions having Bloch symmetry, i.e. obtained by disregarding the core hole. For both the main band and the satellite spectra the Fermi edge singularity was included in the theoretical spectra. Note, however, that in order to obtain agreement with experiment near the Fermi edge, the exponent of the power-law singularity had to be reduced from the value predicted by XPS experiments²¹ on

the basis of current theory²². The required reduction is quite large for the main band, but in the case of the satellite the broadening is too large for any definite conclusion to be drawn. The reason for this discrepancy is at present unknown and suggests that the current theory of x-ray edges may need to be refined. In Sec. 5 we also discuss the implications of the Final State Rule for the interpretation of emission spectra in simple metal alloys. In Sec. 6 we give our conclusions and state our conviction that the same mechanism, proposed here for sodium, is responsible for the "mystery" structure seen in the KLV spectra of all simple metals.

2. Effective one-particle theory of KLV Auger transitions.

In this section we will derive a general formula for the KLV Auger intensity in a solid. We will start with quite general expressions which are then simplified by approximations which will be discussed as they are introduced. We consider the initial state of the Auger process to be the fully relaxed quasi ground state of the many-body system with N electrons and a core hole in the K-shell on a particular site in the solid, i.e. we write

$$|i\rangle = |N;K\rangle \quad (1)$$

This approximation assumes that none of the excitations which were created together with the core hole remain in the vicinity of the hole. Thus, effects of incomplete relaxation which may show up as e.g. plasmon gain satellites²³ are neglected, but these effects are known to be very small^{24, 25}. The approximation also assumes the occupation number of the K-shell to be a good quantum number, i.e. all terms responsible for the Auger and radiative decay of the hole are excluded from the total Hamiltonian. Some of these decay terms will of course reappear later in the transition operator responsible for the particular Auger process of interest here. However, as shown by Almbladh and Minnhagen²⁶, all the terms responsible for the decay of the K-hole can easily be

accounted for by convoluting the final spectrum with an appropriate Lorentzian broadening function. The final state of the the KLV process will be approximated by a product of a one-particle state representing the outgoing Auger electron (labeled A) and some excited state (labeled s) of the many-body system with N-1 electrons and a hole in the L-shell on the same site as the original K-hole, i.e. we write

$$|f\rangle = a_A^+ |N-1, s; L\rangle \quad (2)$$

In this approximation it is assumed that we may neglect the interaction between the outgoing electron and the system left behind. Thus, the Auger electron does not interact with the hole in the valence sea, nor does it suffer any losses due to extrinsic plasmons or particle hole pairs. We also disregard the fact that the Auger electron has to pass a surface in order to escape from the crystal. The approximation (2) is quite analogous to that which leads to a description of the valence XPS experiment in terms of the one-electron Green's function (sometimes referred to as the sudden approximation). The approximation should be rather accurate²⁷ considering the high energy (~ 1 keV) of the Auger electrons considered here, at least if we are not particularly interested in the satellite structure accompanying the parent Auger band. In writing the final state as in Eq. (2) we have also implicitly neglected all terms in the total

Hamiltonian which cause a decay of the L-hole, but this can again be corrected for by convoluting the spectrum with a Lorentzian of a width equal to the inverse life time of the L-hole.

The operator T which is responsible for the KLV transition can be written as

$$T = \sum_{A,V} \langle A,K | v | L,V \rangle a_A^\dagger a_K^\dagger a_V a_L \\ + \sum_{A,V} \langle A,K | v | V,L \rangle a_A^\dagger a_K^\dagger a_V a_L$$

where the labels A, V, K , and L refer to the Auger electron, a valence electron, and the electrons in the K and L shells, respectively. The matrix elements are those of the Coulomb interaction $v(\underline{r}, \underline{r}') = 1/|\underline{r} - \underline{r}'|$. We now obtain the unnormalized KLV Auger intensity from the usual Golden Rule expression

$$I(\omega) = \sum_{A,L,s} |\langle N-1,s;L | a_A^\dagger | N;K \rangle|^2 \\ \cdot \delta(\epsilon_A + E_S(N-1;L) - E_O(N;K)) \cdot \delta(\omega - \epsilon_A) \quad (3)$$

The sums over A , L , and s represent a sum over possible final states. The escaping Auger electron can have different angular momentum symmetries and spins and different energies, and the hole in the L -shell can have different spins and different magnetic quantum numbers. Implicit is also an average over the spin of the K -hole.

The energy of the escaping Auger electron is ϵ_A , and $E_0(N;K)$ is the energy of the quasi ground state of the solid with a hole in the K-shell on a given site. The quantity $E_s(N-1;L)$ is the energy of an excited state s of the solid with $N-1$ electrons and a core hole in the L-shell. The Dirac delta-function, $\delta(\omega - \epsilon_A)$, accounts for the fact that the Auger electrons are analyzed according to their energy but not according to their momentum (or angle of detection). If we assume a negligible content of one-particle states of very high energy (ϵ_A) in the many-electron wave function $|N;K\rangle$, the matrix element becomes

$$\sum_V \langle N-1, s; L | a_K^\dagger a_V a_L | N; K \rangle \{ \langle A, K | v | L, V \rangle - \langle A, K | v | V, L \rangle \}$$

The sum over V is restricted to valence states, i.e. no core states are included (this would result in e.g. KLL transitions which are not of interest here), and we see that the core electrons K and L play a very passive role in the Auger process. They have no internal structure, which means that they have no dispersion and therefore they do not recoil, they are infinitely long lived, and they are distinguishable from the valence electrons, i.e. the core-valence exchange is negligible. Thus, they only act to switch the potential acting on the valence electrons from the potential of a K -hole in the initial state to that of an L -hole in the final state. At this stage we introduce the equivalent core approximation, i.e. we will consider the potentials from the two different core holes to be equal. This is a very accurate

approximation as was shown by Almbladh and von Barth¹⁸. As a consequence of this approximation there will be no Mahan-Nozières-DeDominicis singularity^{28, 22} at the Fermi edge because there is no sudden change of the core hole potential from the initial to the final state. This, of course, is in accordance with the experimental findings^{1, 2, 3} (a possibly very weak effect would not survive the broadening). With the equivalent core approximation the KLV Auger intensity becomes

$$I(\omega) = \sum_{A,L,s} \sum_{V,V'} \langle N\tilde{~} | a_V^\dagger | N-1, s\tilde{~} \rangle \langle N-1, s\tilde{~} | a_V | N\tilde{~} \rangle \\ \cdot M_{KLV}^*(A) \cdot M_{KLV}(A) \cdot \delta(\epsilon_A + \tilde{\omega}_s - \epsilon_F - \epsilon_L + \epsilon_K) \cdot \delta(\omega - \epsilon_A) \quad (4)$$

where the KLV Auger matrix element $M_{KLV}(A)$ is given by

$$M_{KLV}(A) = \langle A, K | \tilde{v} | V, L \rangle - \langle A, K | \tilde{v} | L, V \rangle \quad (5)$$

The tilde ($\tilde{~}$) designates the fact that the valence electrons experience both the periodic lattice potential and an additional impurity potential from one core hole on one site in the solid. This fact, which comes out quite naturally from the above analysis, will prove to be the major ingredient in the explanation of the "mystery" peaks in the experimental spectra. In Eq. (4) we have also

written the total energies $E_s(N-1;L)$ and $E_o(N;K)$ in terms of the negative binding energies ϵ_K and ϵ_L of the K and L holes,

$$E_o(N;K) = E_o(N) - \epsilon_K$$

$$E_o(N-1;L) = E_o(N) - \epsilon_F - \epsilon_L$$

$$\tilde{\omega}_s = \tilde{E}_s(N) - \tilde{E}_o(N)$$

where ϵ_F is the Fermi energy, which is unchanged by a core hole, $\tilde{E}_o(N)$ and $E_o(N)$ are the ground state energies of the solid with and without a core hole, and $\tilde{\omega}_s$ is an excitation energy of the N-electron system with one core hole. Making use of the definition of the one-hole spectral function of the valence electrons ²⁹, $A_{VV'}(\omega)$, Eq. (4) can be simplified further giving

$$I(\omega) = \sum_{\substack{A,L \\ V,V'}} M_{KLV}^{*}(A) M_{KLV}(A) A_{VV'}(\omega - \epsilon_L + \epsilon_K) \delta(\omega - \epsilon_A) \quad (6)$$

From this expression the close relationship to the XPS experiment in the intrinsic approximation (Eq. (2)) is again clear. The KLV experiment is like a valence XPS experiment performed with an exciting photon energy of $\epsilon_L - \epsilon_K$. This analogy is actually exploited to subtract background from experimental spectra ³. For a detailed

description of the main Auger band one must, however, consider the fact that the dipole coupling to the radiation field in XPS is replaced by a Coulomb matrix element in the Auger case, and, more importantly, this Coulomb matrix element is to be calculated with one-particle wave functions obtained in the presence of a core hole. A further difference between the two experiments is that the spectral function of the valence holes in Eq. (6) should, in principle, also be evaluated in the presence of a core hole. This distinction is, however, irrelevant in the present work since we here intend to replace the interacting spectral function with that of non-interacting holes,

$$A_{VV}(\omega) = \delta_{VV} \cdot \delta(\omega - \epsilon_V) \cdot \theta(\epsilon_F - \epsilon_V) \quad (7)$$

Here, ϵ_V is a valence-hole energy and θ is the usual step function restricting holes to be below the Fermi level ϵ_F . In this way we disregard all intrinsic satellite structure and concentrate on the parent Auger band whose overall shape, we hope, is only slightly affected by valence-valence interactions. This hope is based on our experience from x-ray emission experiments on simple metals. These experiments are quite well described in terms of the transient one-particle theory of Nozières and DeDominicis²² in which the valence-valence interaction is neglected. The emission experiments will be described in Sec. 5. It should be noted that - as far as the satellite structure is concerned - no accuracy is to

be gained by retaining the interacting spectral function in Eq. (6). This would account for the intrinsic losses but by writing our final states as in Eq. (2), we have already neglected all extrinsic losses which are equally important in simple metals^{6, 30, 31}. Within the main band the interaction will mainly act to reduce the strength of the quasi-particle peak, broaden it, and give it a slight asymmetry^{29, 32}. None of these effects are expected to give any structure to the band, the dominant effect being the quasi-particle broadening, which will be included at the end, as discussed in Sec. 4. Inserting the non-interacting spectral function (Eq.(7)) into Eq.(6), we arrive at our effective one-electron description of the KLV Auger spectrum

$$I(\omega) = \sum_{A,L,V} |M_{KLV}(A)|^2 \delta(\omega - \epsilon_L + \epsilon_K - \epsilon_V) \delta(\omega - \epsilon_A) \theta(\epsilon_F - \epsilon_V) \quad (8)$$

It now remains to evaluate the Coulomb matrix elements $M_{KLV}(A)$ with the one-particle wave functions obtained in the presence of the core hole, and this task involves some further approximations. Within the central cell (atomic sphere) containing the core hole we write the wave functions as

$$\psi_K(\underline{r}) = R_K(r) Y_{L_K}(\hat{r}) \quad (9)$$

$$\psi_L(\underline{r}) = R_L(r) Y_{L_L}(\hat{r}) \quad (10)$$

$$\psi_V(\underline{r}) = \sum_L c_L(k_V) R_L(\epsilon_V, r) Y_L(\hat{r}) \quad (11)$$

$$\psi_A(\underline{r}) = \left(\frac{v_{\ell_A}(\epsilon_A)}{2(2\ell_A+1)} \right)^{\frac{1}{2}} R_{\ell_A}(\epsilon_A, r) Y_{L_A}(\hat{r}) \quad (12)$$

where L is short for (l, m) . All radial wave functions $R(r)$ are normalized to unity over the Wigner-Seitz sphere of radius S ,

$$\int_0^S R^2(r) r^2 dr = 1 \quad (13)$$

Due to the strong damping of quasi-particles²⁹ at energies much above the Fermi energy, the bandstructure at these high energies becomes less relevant. Therefore, we have chosen to approximate the wave function of the outgoing Auger electron by a free spherical wave outside the Wigner-Seitz sphere. In this way, the Auger electron feels the full potential of the central cell with the core hole, but outside it is unaffected by the periodic potential of the surrounding lattice. This means, e.g., that it cannot be backscattered from the neighboring atoms which precludes the possibility of seeing any extended x-ray absorption fine structure (EXAFS) in the Auger spectrum. However, at the large Auger energies considered

here (~ 1 keV), the distance in energy between successive maxima in the EXAFS is much larger than the valence band width. The back-scattering effect will thus not give rise to any structure in the Auger spectrum. Only the absolute intensity of the spectrum may be slightly affected (typically by less than 5%)^{33, 34}. A further consequence of the spherical approximation for the Auger electron is that we cannot account for the fact that only those electrons emitted into a certain solid angle can reach the surface and escape into the vacuum to be detected. The escape depth of keV electrons is, however, relatively large ($\sim 40\text{\AA}$ ^{35, 36}), most electrons originate from the bulk and surface effects are therefore negligible in the present context. The wave function of the Auger electron has been chosen to be δ -function normalized in the energy variable, i.e.

$$\int \psi_A^* \psi_A d^3r = \delta_{L_A, L_A'} \cdot \delta(\epsilon_A - \epsilon_{A'}) \quad (14)$$

This implies that the radial wave function

$$\left[\frac{v_{\ell_A}(\epsilon_A)}{2(2\ell_A + 1)} \right]^{\frac{1}{2}} \cdot R_{\ell_A}(\epsilon_A, r) \quad \text{and its derivative}$$

have to be matched continuously at the Wigner-Seitz radius S to a free electron wave function of the form

$$\left(\frac{k_A}{\pi} \right)^{\frac{1}{2}} \cdot \left(\cos \delta_{\ell_A} \cdot j_{\ell_A}(k_A r) - \sin \delta_{\ell_A} \cdot n_{\ell_A}(k_A r) \right) \quad \text{Here, } j_{\ell} \text{ and } n_{\ell} \text{ are the regular and irregular spherical Bessel}$$

functions³⁷ and the wave vector k_A is given by $\sqrt{\epsilon_A}$. This matching condition determines the local state density $\mathcal{D}_\ell(\epsilon)$ of each angular momentum channel as well as the phase shifts δ_ℓ . Since the overlap of core electron wave functions centered on adjacent sites is negligible, we can from the outset single out a particular site which is associated with the core hole and which can be considered as the origin of the Auger electron.

With the approximations presented above it is straightforward to obtain a relatively simple expression for the Auger matrix element $M_{KLV}(A)$, which, according to Eq. (8), has to be squared and summed over degenerate final states. Assuming equal probabilities for the excitation of degenerate initial states, we must also average over their quantum labels. In Appendix 1 we derive the following result for the Auger intensity

$$\begin{aligned}
 I(\epsilon_A) = & \frac{1}{2}(\ell_L + 1) \sum_{\ell_A, \ell_V} \left(\begin{matrix} \ell_A & \ell_V & \ell_L \\ 0 & 0 & 0 \end{matrix} \right)^2 \mathcal{D}_{\ell_A}(\epsilon_A) \cdot \mathcal{D}_{\ell_V}(\epsilon_A - \epsilon_L + \epsilon_K) \\
 & \cdot \rho(\epsilon_F - \epsilon_K + \epsilon_L - \epsilon_A) \\
 & \cdot \left[\bar{R}_{\ell_L}^2(A, K; \ell_V, L) + \bar{R}_{\ell_V}^2(A, K; L, \ell_V) \right. \\
 & \quad \left. - \bar{R}_{\ell_L}(A, K; \ell_V, L) \cdot \bar{R}_{\ell_V}(A, K; L, \ell_V) \right]
 \end{aligned}
 \tag{15}$$

where the local partial density of states is defined in

the usual way

$$\begin{aligned}
 \mathcal{D}_{\ell}(\varepsilon_A) &= \sum_{V(\ell_V=\ell)} \int_0^S |\psi_V(\underline{r})|^2 d^3r \delta(\varepsilon_A - \varepsilon_V(\underline{k}_V)) \\
 &= \sum_{\sigma_V, m_V} \sum_{\underline{k}_V} |c_{L_V}(\underline{k}_V)|^2 \delta(\varepsilon_A - \varepsilon_V(\underline{k}_V)) \quad (16)
 \end{aligned}$$

and where the radial integrals $R_{\ell}(a, b; c, d)$ are defined in Appendix 1. (Eq. (A1.5), $\bar{R} = R/(2l+1)$). In order to avoid band indices in Eqs. (11) and (16), we consider $\underline{k}$ -vectors of the extended zone scheme. Note that the valence wave function ψ_V is an impurity wave function. It can, however, still be labeled by a wave vector of the periodic solid because there is a one-to-one correspondence between the Bloch functions and the impurity wave functions. Note also that the partial state densities $\mathcal{D}_{\ell_A}(\omega)$ and $\mathcal{D}_{\ell_V}(\omega - \varepsilon_L + \varepsilon_K)$ in Eq. (15) are the local densities in the central cell and are therefore strongly affected by the presence of the core hole. This will be the single most important ingredient in the explanation of the Auger spectra.

We end this section with a few comments on Eq. (15). In a simple metal there are essentially only s and p electrons below the Fermi level, i.e. ℓ_V is either 0 or 1. In the case of the KL_1V spectrum ℓ_L is 0 and therefore ℓ_A equals ℓ_V , i.e. an s-like (p-like) valence electron gives rise to an s-like (p-like) Auger electron. Anticipating the calculations described in the Sec. 3, we have found empirically that

$$\mathcal{D}_{\ell_A}(\epsilon_A) \cong C \sqrt{\epsilon_A} \cdot (2\ell_A + 1) \quad (17)$$

where C (~ 0.017) is almost independent of both the angular momentum quantum number ℓ_A and the energy ϵ_A over a range corresponding to the width of the valence band. Thus, for the KL_1V case, Eq. (15) reduces to

$$I_{KL_1V}(\epsilon_A) = \frac{1}{2} C \sqrt{\epsilon_A} \{ A_s \cdot \mathcal{D}_s(\epsilon_V) + A_p \cdot \mathcal{D}_p(\epsilon_V) \} \quad (18)$$

where the valence energy ϵ_V is determined by the energy ϵ_A of the Auger electron according to $\epsilon_V = \epsilon_A - (\epsilon_L - \epsilon_K)$. The coefficients A_s and A_p are determined by the Clebsh-Gordon coefficients and by the radial matrix elements within the brackets of Eq. (15). The factor $\sqrt{\epsilon_A}$ obviously has a slow variation over a valence band width, and from our numerical calculation we find that this is also true for the coefficients A_s and A_p . Thus, the KL_1V Auger spectrum gives a picture of the occupied valence band which is determined by a particular weighting of its s and p components. This weighting depends on the numerical values of a number of Coulomb matrix elements and is not only determined by Clebsh-Gordon coefficients as was erroneously stated in Ref. 3. Numerically, A_s turns out to be approximately three times larger than A_p , $A_s \sim 3 A_p$, and we can then write the KL_1V spectrum as

$$I_{KL_1V}(\epsilon_A) = A_0 \{ \mathcal{D}_s(\epsilon_V) + 1/3 \mathcal{D}_p(\epsilon_V) \} \quad (19)$$

where A_0 is a slowly varying factor.

The analysis of the $KL_{2,3}V$ spectrum is slightly more complicated because, when $\ell_L = 1$, there are three terms in Eq. (15). The $3j$ -symbol in Eq. (15) gives rise to selection rules of dipole character, such that s in the valence band couples to p in the Auger continuum and p in the valence band produces Auger electrons of both s and d character, although the d -channel is the dominant channel. According to this analysis, the $KL_{2,3}V$ spectrum is also a weighted sum of the local s and p valence state densities. In this case, however, we find numerically that both partial densities enter with approximately equal weights. We thus obtain the following simple result for the $KL_{2,3}V$ intensity

$$I_{KL_{2,3}V}(\epsilon_A) = A_1 \{ \mathcal{D}_s(\epsilon_V) + \mathcal{D}_p(\epsilon_V) \} \quad (20)$$

where again A_1 varies slowly over the band.

A rough check on the accuracy of the radial matrix elements can be obtained from the relative intensities of the KL_1V and $KL_{2,3}V$ Auger lines of the free sodium atom. In these spectra only one valence electron - the $3s$ electron in the M shell - is involved. Thus, if we ignored the fact that our matrix elements are obtained from wave

functions of the solid and not of the free atom, we would predict a $KL_{2,3}^M$ to KL_1^M intensity ratio of $A_1 / A_0 \sim 1.3$ in the free atom. The experimental result for this ratio is 1.4^{38} , which gives us some confidence in the results obtained. Perhaps a more stringent test is to compare the ratio between our integrated $KL_{2,3}^V$ and KL_1^V intensities directly with the corresponding experimental data for the solid². For a rough estimate we need the total number of s and p electrons (n_s and n_p) in the central cell around the impurity for which we obtain

$$n_s = \int_{-\infty}^{\epsilon_F} \mathcal{D}_s(\epsilon_V) d\epsilon_V = 1.16 \quad (21)$$

$$n_p = \int_{-\infty}^{\epsilon_F} \mathcal{D}_p(\epsilon_V) d\epsilon_V = 0.76 \quad (22)$$

Integrating Eqs. (19) and (20) over the occupied part of the valence band and using the above numbers we find a $KL_{2,3}^V$ to KL_1^V intensity ratio of 1.8 in the solid. we find this simple estimate to be in close agreement with our exact result given in Sec. 4. The experimental result for this ratio is 2.0 ± 0.2^2 , the agreement again appears to be quite reasonable.

3. The self-consistent repeated-cluster method for impurities.

As stressed in the previous sections, a reliable description of KLV spectra requires the wave functions of the valence and Auger electrons obtained from a potential that includes the core hole (Eq. (15)). We thus have a self-consistent impurity problem at our hands. There now exist powerful programs^{39, 40, 41} for solving such a problem with the same speed and efficiency as are common to modern self-consistent bandstructure programs. When the present work was started in 1975, these new efficient methods had, however, not yet been worked out. As we at the time were developing bandstructure programs based on the very efficient Linear Muffin-Tin Orbital method (LMTO) introduced by O. K. Andersen⁴², we decided to solve the impurity problem by doing repeated cluster calculations. While this approach is not tailor-made for the impurity problem per se, it has the advantage of being directly applicable to more complex systems such as compounds and ordered alloys. For the core hole problem this method implies that the solid is divided up into equal units (clusters), each containing a given number of atoms. In each cluster we then introduce one or more core holes on a certain atom. Taking this cluster as the unit cell of the perturbed system, we have artificially restored translational symmetry. The advantage of this approach is that the electronic structure of this system can be

obtained from ordinary band theory, albeit with a large number of atoms per unit cell. The case of interest here, i.e. an isolated excited atom in an otherwise perfect host crystal, represents the limit of very large clusters. It should be remembered that we are only interested in the local properties of the cluster close to the core hole and thus the size of the cluster must only be large enough that the effect of all other core holes on a particular excited atom can be neglected. Unfortunately, the number of atoms per unit cell and therefore the size of the secular matrix increases rapidly with cluster size. We found, however, that calculations for unit cells containing 16 atoms, one atom with a core hole surrounded by 15 ground state atoms, represented a reasonable compromise between accuracy and computational feasibility, as will be discussed below.

In spite of the efficiency of the LMTO method, a self-consistent bandstructure calculation with 16 atoms per unit cell would still have been rather cumbersome, had it not been possible to drastically reduce the computational effort in achieving self-consistency. This reduction was made possible by the Spherical Solid Model (SSM) developed by Almladh and von Barth¹⁸. The SSM actually proved capable of producing rather accurate self-consistent potentials for an atom in a simple metal with zero, one or two core holes. A full account of the SSM can be found in Ref. 18; here we only give the basic ideas and formulae needed to understand the computational aspects of the present work.

The electron density $n(\underline{r})$ of a homonuclear solid with one atom per unit cell is determined by the self-consistent set of equations ⁴³

$$\{ -\nabla^2 + V(\underline{r}) \} \varphi_k(\underline{r}) = \epsilon_k \varphi_k(\underline{r}) \quad (23a)$$

$$V(\underline{r}) = -Z \sum_{\underline{\ell}} v(\underline{r}-\underline{\ell}) + \int v(\underline{r}-\underline{r}') n(\underline{r}') d^3 r' + v_{xc}(\underline{r}) \quad (23b)$$

$$n(\underline{r}) = \sum_{\epsilon_k < \epsilon_F} |\varphi_k(\underline{r})|^2 \quad (23c)$$

$$N = \sum_{\epsilon_k < \epsilon_F} 1 \quad (23d)$$

Here, $v(\underline{r}) = 2/r$ is the Coulomb interaction, Z is the nuclear charge, N the total number of electrons, ϵ_F the Fermi energy (defined by. Eq.(23d)), $\underline{\ell}$ a lattice vector, and we use Bohr radii and Rydbergs as units for lengths and energies. In the commonly used local-density approximation, which is rather accurate ^{44, 45} as far as charge densities are concerned, the exchange-correlation potential $v_{xc}(\underline{r})$ is given by ⁴³

$$v_{xc}(\underline{r}) = \mu_{xc}(n(\underline{r})) \quad (24)$$

where $\mu_{xc}(n)$ is the contribution from exchange and correlation to the chemical potential of the homogeneous electron gas of density n . The Eqs. (23a-d) represent the self-consistent bandstructure problem, but if we are only

interested in the electron density in the central cell at the origin, the problem can be simplified considerably without any significant loss of accuracy. We begin by dividing the total density into a core electron contribution $n_c(\underline{r})$ and a valence electron contribution $n_v(\underline{r})$. Defining an ionic potential $w_{ion}(\underline{r})$ by

$$w_{ion}(\underline{r}) = -Zv(\underline{r}) + \int_{\Omega_0} v(\underline{r}-\underline{r}') n_c(\underline{r}') d^3r' , \quad (25)$$

where Ω_0 is the volume of the central cell, the total potential $V(\underline{r})$ can be written

$$V(\underline{r}) = w_{ion}(\underline{r}) + \int v(\underline{r}-\underline{r}') n_v(\underline{r}') d^3r' + \mu_{xc}(n(\underline{r})) + V_s(\underline{r}) \quad (26)$$

where $V_s(\underline{r})$ is the potential from all ions surrounding the central cell,

$$V_s(\underline{r}) = \sum_{\underline{\ell} \neq 0} w_{ion}(\underline{r}-\underline{\ell}) \quad (27)$$

It is intuitively clear, that the potential $V_s(\underline{r})$ varies relatively slowly in the central cell and therefore, it cannot significantly affect the shape of the electron density in that cell. This is the basic assumption behind the SSM, which is obtained by first replacing the surrounding ions ($w_{ion}(\underline{r}-\underline{\ell})$, $\underline{\ell} \neq 0$) by pseudoions ($w_{ps}(\underline{r}-\underline{\ell})$, $\underline{\ell} \neq 0$) and then retaining only the spherical average of the resulting potential $V_s(\underline{r})$,

$$V_S(\underline{r}) \Rightarrow V_S(r) = \int V_S(\underline{r}) \frac{d\Omega}{4\pi} \quad (28)$$

Always assuming a spherical core electron density $n_c(\underline{r})$ ⁴⁶, all terms in the total potential $V(\underline{r})$ in Eq. (26) are spherically symmetric, and we have reduced the complicated band problem to a much simpler problem of a single spherical atom in a spherical solid represented by the fixed potential $V_S(r)$. The spherical self-consistent density $n_{SSM}(r)$ of this problem should be rather close to the true density of the solid in the central cell, but outside, $n_{SSM}(r)$ will slowly tend to the average density of the valence electrons of the solid, i.e. to $n_0 = Z_V/\Omega_0$, where Z_V is the number of valence electrons in the unit cell Ω_0 . There is, however, a problem with the SSM in that the model does not guarantee charge neutrality within the central atomic cell ($\int_{\Omega_0} n_{SSM}(r) d^3r \neq Z_V$), which is an essential feature of the band problem. For this reason and in order to better simulate a charge density of the proper symmetry, we construct the total crystal density by superposing SSM densities according to

$$n(\underline{r}) = n_0 + \sum_{\underline{\ell}} \{ n_{SSM}(|\underline{r}-\underline{\ell}|) - n_0 \} \quad (29)$$

From this approximate, self-consistent density it is straightforward to obtain the self-consistent crystal potential using Eqs. (23b) and (24) and the self-consistent local-density bandstructure from Eq. (23a). There is, however, a minor numerical difficulty associated with the construction implied by Eq. (29). The density

$n_{SSM}(r) - n_0$ tends to zero approximately as r^{-3} for large r and, therefore, the sum in Eq. (29) converges very slowly. Sometimes it is possible to obtain a more rapidly convergent series by converting the sum in real space into a sum in reciprocal space via Fourier transforms. In the present case this technique is not directly applicable because the SSM density has rapid oscillations in the core region and thus will yield a Fourier transform with appreciable amplitude at relatively large wave vectors. Consequently, the sum in reciprocal space also converges rather slowly. If, however, the SSM density first is divided into a rapidly varying, but short-range part n_{in} and a slowly varying, long-range part n_{out} according to

$$n_{in}(r) = \{n_{SSM}(r) - n_0\} e^{-r^2/r_0^2} \quad (30)$$

$$n_{out}(r) = n_{SSM}(r) - n_0 - n_{in}(r) \quad (31)$$

it becomes numerically convenient to sum the short-range parts in real space and the long-range parts in reciprocal space. The radius r_0 can be chosen to obtain optimal convergence of both sums simultaneously, and we have found that one third of the Wigner Seitz radius is a convenient choice which makes it possible to retain only the first term of the sum in real space.

The accuracy of our procedure for constructing an approximate, self-consistent band structure potential for the solid was checked as follows. We computed the bandstructure of lithium using the LMTO method⁴² in the Atomic Sphere Approximation (ASA) and found our result to be essentially identical to the bandstructure obtained by Rudge⁴⁷ in his self-consistent calculation. The two bandstructures differed by less than 5 mRy below the Fermi energy. The ASA should give errors of comparable magnitude as the muffin-tin approximation. Errors due to the latter are, however, according to Rudge, below the mRy level. Rudge performed fully self-consistent calculations with exchange only (μ_{xc} replaced by μ_x , the exchange contribution to the chemical potential of the electron gas, in Eq. (24)), but the difference between self-consistent bandstructures obtained with exchange only (μ_x) or with full exchange-correlation (μ_{xc}) is known to be small⁴⁸. We thus conclude that the electron density constructed from superposed SSM densities is very nearly the same as that obtained from a fully self-consistent band structure calculation.

Our next step was to construct the charge density for the case of one or two core holes on a particular atom in the solid. Within the SSM it is a straightforward matter to reduce the occupation number of a particular core orbital by one or two units and then, once again, to carry the calculation to self-consistency. Note, that all core orbitals are free to adjust during the self-consistency loop, as they were in the ground state

calculation with all core orbitals occupied. Density-functional theory can, in principle, only be used to calculate ground-state densities. The state with a core hole can, however, be considered as the ground state of a different Hamiltonian, and the theory should therefore also give an accurate density for the fully relaxed quasi-ground state of a hypothetical spherical solid from which a core electron has been removed from the center¹⁸. Furthermore, due to the short screening length of the electron gas⁴⁵, we expect the potential outside the central cell to have a very minor effect on the density screening the core hole. Therefore, we expect $n_{SSM}^{(v)}(\underline{r}) - n_{SSM}^{(o)}(\underline{r})$ to give an accurate representation of the screening cloud also in the anisotropic solid - at least within the central atomic sphere - (by $n_{SSM}^{(v)}(\underline{r})$ we mean the self-consistent SSM density with v core holes at the center). We can then assume that the charge density $n^{(v)}(\underline{r})$ of the solid with v core holes on one of its atoms is given accurately by

$$n^{(v)}(\underline{r}) = n(\underline{r}) + n_{SSM}^{(v)}(\underline{r}) - n_{SSM}^{(o)}(\underline{r}) \quad (32)$$

where $n(\underline{r})$ is the ground state density obtained from Eq. (29).

Considering now the construction of an approximately self-consistent potential for a solid made up of repeated clusters containing one atom with a core hole surrounded by ground state atoms, we note that, due to the short screening length of the electron gas⁴⁵, the

clusters do not have to be very large (i.e. only have to contain a rather small number of ground state atoms), before the potential in the central cell around the excited atom is almost equal to what it would have been in the case of a single excited atom in an infinite solid. In other words, as far as electron densities and potentials are concerned, the relevant limit of infinite dilution is reached at moderately large cluster sizes. We thus have strong reasons to believe that a fully self-consistent potential of such a cluster is quite accurately approximated by taking the density in the atomic sphere of the excited atom to be given by Eq. (32) and the density in the atomic spheres of the surrounding ground state atoms to be given by Eq. (29)

We tested this assumption on our largest cluster containing one excited sodium atom with a hole in the 2p-shell and 15 ground state sodium atoms. From the potential constructed as described above, we calculated the band structure and the wave functions of the solid made up of repeated clusters. Summing the charge in each atomic sphere, we found all spheres to be closely neutral, the sphere of the excited atom contained 1.96 electrons while for all ground state atoms the valence charge differed by less than 0.015 from unity. From these densities we constructed a new potential and repeated the band calculation. We found that the two bandstructures differed by less than 6 mRy below the Fermi energy, which indicated that we had obtained a self-consistent solution to the cluster problem. The impurity potential obtained within

the SSM, which only includes the surrounding lattice in a spherically averaged way, was thus almost identical to that obtained from the repeated cluster calculation with relatively few atoms per unit cell. This congruence cannot be a coincidence, but is rather a reflection of the fact that both methods had converged towards the limit of an isolated impurity within an infinite host.

Our next step was to construct the partial state densities for the excited cell of the cluster. Since the electron densities and potentials of the SSM are in fact locally rather close to the corresponding quantities in the solid, both with and without core holes, it would, at this point, be quite relevant to ask why the local partial state densities could not be obtained directly from the SSM. The answer is that spectral properties are poorly described by the SSM as was discussed in Ref. 18. The spherical shells outside the central cell in the SSM appear to scatter electrons much more strongly than do the surrounding ions on the lattice of a real solid. As a result, the number of electrons of s and p character in the central cell is different in the SSM as compared to a real solid and this difference is more pronounced in the presence of a core hole. Thus, local spectral properties are much more sensitive quantities than charge densities or potentials. Therefore, the partial state densities had to be obtained from the cluster calculation. Regarding spectral properties, we may consider the width of the occupied part of the band as a criterion for convergence towards the limit of infinite dilution. Clearly a

localized impurity in an infinite solid cannot change this width. The introduction of a superlattice of "impurities", i.e. atoms with core holes, will, however, change the width, higher concentrations giving larger band widths. The number of ground state atoms had to be made large enough for this change in width to be negligible for our purposes. We found that for 16 atom supercells with one core hole the bandwidth changed by at most 7% from its ground state value for both sodium and lithium. Furthermore, the resulting global state densities agreed rather closely with their ground state counterparts.

The bandstructure was calculated using the LMT0 method ⁴² within the ASA, the latter being of comparable accuracy as the better known muffin-tin approximation. The wave functions in the LMT0 method are set up as a linear combination of Bloch sums of Muffin Tin Orbitals (MTO's). These MTO's are centered on atomic sites and have a definite angular momentum (l,m) character. The size of the resulting secular matrix then depends on the number of atoms within the unit cell and on the angular momentum at which the expansion of the wave function is truncated. In the 16 atom cluster calculation we included MTO's up to l=2 on the impurity but only s and p MTO's on the surrounding sites. Neglecting d functions on the ground state atoms decreased the dimension of the secular matrix from 144 to 69, greatly reducing the numerical effort, but had only a marginal effect on the state densities. This was checked in sodium by replacing the impurity by a ground state potential and comparing the resulting partial

state densities of the central cell with those of pure sodium obtained from an ordinary band calculation with one atom per unit cell, including d functions. The approximation of using a restricted basis set overestimated the local partial state densities on the central site, the error increasing from zero at the bottom of the band to at most 6% at the Fermi energy⁴⁹. This error was the price for a substantial reduction in computer time.

In our 16 atom supercell calculation the impurities were distributed on a simple cubic lattice, with a lattice parameter twice that of sodium. Fig. 1 shows the cubic Brillouin zone (BZ) corresponding to this supercell, together with the Brillouin zone of the bcc-lattice of the ground state metal, whose volume is 16 times larger. In Fig. 2 we have plotted the bands along a (100)-direction obtained for the 16 atom supercell for the three cases: the "impurity" is a ground state atom (a), or an atom with one (b) or two (c) core holes. The bands in (a) were actually obtained by folding the lowest band of pure sodium, which is nearly parabolic in the larger bcc-Brillouin zone, into the smaller supercell BZ. These bands were identical to the result of the 16 ground state atom cluster calculation, if we overlook the small errors induced by the more limited basis set of the latter. When describing the crystal structure of sodium in terms of this larger supercell, one only takes into account a subgroup of the full space group, thus accidental degeneracies are to be expected along all symmetry lines.

As core hole potentials are introduced at the corners of the cubic supercell, the symmetry is lowered, all accidental degeneracies are split and bandgaps open up at the BZ-faces. Fig. 2 exaggerates this effect somewhat, in that the shifts are largest along and near symmetry directions, the contribution of these regions to the state densities is, however, rather limited. In case (b) each supercell now must contain 17 electrons, including the one screening the core hole, which is found to be essentially localized at the excited atom. Compared to the ground state cluster calculation, the Fermi energy remains the same while the bottom of the band is lowered by 15 mRy. As mentioned above, this calculation was found to be well converged with respect to self-consistency.

A second core hole in the 2p-shell, Fig. 2c, strongly distorts the bands, a bound state appears. Its binding energy was estimated to be about 50 mRy below the bottom of the ground state band, in good agreement with the value of 45 mRy found in the corresponding SSM calculation¹⁸. The supercell of 16 atoms is, however, too small to contain a bound state and to let the higher bands reconstruct the global state density of sodium. As this system will not interest us further, no attempt was made to enlarge the cluster.

The bands were calculated at 54 k -points in the irreducible wedge of the BZ, which corresponds to using 864 points in the irreducible wedge of the larger bcc-BZ of the ground state metal. From the energy-eigenvalues and

wave functions we then obtained the global and partial state densities (Eq. (16)) approximately by replacing the sum of delta-functions by a sum of Gaussians, whose widths were chosen proportional to the average energy separation between states lying in the same band and belonging to adjacent k -points. This procedure will tend to smoothen structure in the state densities, especially for higher energies, but for our purpose it would anyhow have been quite irrelevant to resolve any detailed structure associated with supercell bandstructure effects.

The supercell calculation was intended as an approximation to the dilute limit. Both eigenvalues and wave functions will contain spurious effects due to the superlattice of impurities. The eigenvalues of the dilute limit are given by those of the infinite, pure host metal. This fact suggests an approximate short-cut towards the dilute limit. We replace the cluster eigenvalues by those of the pure metal, while we use the cluster wave functions to obtain the local spectral properties. This procedure yields the correct bandwidth while only marginally affecting the spectral shape of the local state densities. In Fig. 3 we see that the local density of states for the atom containing a core hole has changed drastically from the ground state DOS. We find a significant localization of s - electrons near the bottom of the band, while the DOS of the p - electrons is rather uniformly enhanced. It is this distortion that will significantly affect both the KLV Auger spectra and the $L_{2,3}\text{SXE}$ satellites.

4. KLV Auger spectra of sodium.

In this section we present our results for the KLV spectra of sodium obtained by a direct numerical evaluation of Eq. (15). The radial parts of all wave functions involved in the radial matrix elements $\bar{R}_\ell(a,b;c,d)$ were obtained by integrating the radial Schrödinger equation out to the Wigner-Seitz radius S , using the spherically averaged impurity potential corresponding to a sodium atom with a self-consistently screened 2p core hole in the infinite solid. At the energy ϵ_A of the outgoing Auger electron we obtained the local partial state densities at the site of the core hole, $\mathcal{D}_\ell(\epsilon_A)$, by matching the solution of the radial Schrödinger equation inside the Wigner-Seitz sphere to a delta-function normalized free spherical wave outside the sphere, as described in Sec. 2. Below the Fermi energy $\mathcal{D}_\ell(\epsilon)$ was obtained in the usual way (Eq. (16)) from our bandstructure calculation for a solid with a unit cell containing one core hole potential and 15 ground state potentials (cf. Sec. 3).

For the evaluation of the radial Coulomb matrix elements we, in principle, need the wave functions in all space. The core wave functions of both the K and the L shells were found to be negligible outside the Wigner-Seitz radius S , a fact which simplifies the numerical calculation. For those matrix elements where the two core

functions have different coordinates, the integrand vanishes beyond S . When the core functions have the same coordinate, the integral with respect to this coordinate has no contributions from outside S . The integral with respect to the second coordinate has, outside the Wigner Seitz sphere, the character of a matrix element of an operator decreasing as r^{-2} or faster, taken between two continuum wave functions. Due to their large energy difference, $\epsilon_A - \epsilon_V$, this contribution is, however, small for s and p electrons. We verified this by augmenting the radial wave functions with free electron spherical waves outside the atomic sphere, where zero energy was defined by the bottom of the band, and then carrying the integrals to convergence with respect to a cut-off radius. This procedure changed matrix elements by less than 5%. This was not true for valence d electrons. However, their matrix elements, augmented as above, turned out to be an order of magnitude smaller than for both s and p electrons, and since the local partial DOS of d character is rather small in sodium anyway, the total valence d contribution was found to be negligible. We were thus confident that the errors in the relevant radial integrals for both s and p valence electrons were less than a few per cent.

Before comparing our results to experiment, we must consider the mechanisms that will broaden the spectrum. Firstly, the spectrum is broadened by a Lorentzian ²⁶ taking the finite life-times of the core holes into account. From core XPS studies, Citrin et al. ²¹ obtained

the FWHM values of 0.28 ± 0.03 eV for the 1s and the 2s levels and 0.02 ± 0.02 for the 2p level of sodium. Secondly, we have to consider the finite energy width of each quasi-particle in the valence band²⁹. At present we know little of the detailed behavior of the valence electron spectral function for a solid²⁷, and even less for a solid with an impurity. To get an estimate of the quasi-particle width we fall back on calculations for a homogeneous electron gas with a density equal to the average density of sodium. For the simple case of an energy-independent self-energy, the energy distribution becomes a Lorentzian with a FWHM equal to twice the imaginary part of the self-energy. The width is, however, state dependent, it is zero at the Fermi-surface and grows approximately quadratically (as $(\epsilon_{\underline{k}} - \epsilon_F)^2$) towards the bottom of the band, where calculations by Hedin⁵⁰ give a value of 0.45 eV for the imaginary part of the self-energy. Due to the rather large uncertainty, however, we allowed the width to vary during the fit to experiment, as it had some influence on the shape of the Auger spectra. The value we finally chose for the FWHM on the basis of both the Auger and the $L_{2,3}$ emission spectra corresponded to an imaginary part of the self-energy of 0.27 eV at the bottom of the band. Finally we also have to include the instrumental broadening by a Gaussian, compared to which we find any phonon broadening²¹ to be negligible.

In Figures 4 and 5 we compare our theoretical spectra with the experimental data reported by Barrie and Street². Taking the core-hole life times, i.e. the

widths of the Lorentzian broadening, as given, we determined the width of the instrumental Gaussian broadening by fitting the Fermi edge to experiment. We obtained a FWHM value of 0.8 eV, while Barrie and Street give 0.9 eV. During the fitting procedure the relative magnitudes of the experimental KL_1V and $KL_{2,3}V$ spectra were also allowed to vary. The ratio obtained from the best fit agrees with experiment in the sense that it is consistent with the remark by Barrie and Street, that the intensity of the "mystery" peaks is almost exactly the same in both KL_1V and $KL_{2,3}V$ spectra, while the "valence band contribution", i.e. the peak near the Fermi edge, is approximately 2.5 times greater for $KL_{2,3}V$. For the ratio of the integrated intensities we find $I(KL_{2,3}V)/I(KL_1V) = 1.8$, which also agrees well with the data recently reported by Lässer and Fuggle³. More importantly, our theory is for the first time able to account for the observed two-peak structure, i.e. attributing the "mystery" peaks near the bottom of the band to the strong localization of s electrons in the presence of the core hole. While both spectra reflect this distortion of the local partial state densities, the difference between the two spectra is a consequence of the different matrix elements. The detailed agreement with experiment may seem somewhat less satisfactory as the intensities of the "mystery" structure relative to the peak near the Fermi edge do not accurately agree with experiment. In view of the fact, however, that the KL_1V spectrum lies on a rapidly varying background, and that also the shape of the $KL_{2,3}V$ spectrum may be strongly

affected by inelastic losses, the experimental uncertainty in this relative intensity must be considerable. Furthermore, we note that the detailed agreement depends on the energy dependent quasi-particle broadening, which is only known rather approximately. Using the value 0.45 eV, given by Hedin⁵⁰ for the imaginary part of the self-energy, would e.g. approximately reduce the strength of the low-energy peak in KL_1V to that of the peak near the Fermi energy. Other neglected many-body effects and approximations in the calculation of the state densities could also produce errors on the 5 - 10% level. Thus both theory and experiment are plagued with uncertainties whose magnitude is comparable to the disagreement between the spectra.

5. SXE main band and satellite spectra.

The main band emission spectrum arises from transitions in which a single core hole is filled by a valence electron. The initial state $|i\rangle$, disregarding incomplete relaxation effects as discussed in Sec. 2, is the fully relaxed many-body system of N valence electrons in the presence of the core hole. The final state $|f\rangle$, on the other hand, is some excited state of $N-1$ valence electrons, but now all core states are filled. From the Golden Rule the emission intensity is, in the dipole approximation, given by

$$I(\omega) = C\omega \sum_f |\langle i | \underline{p} | f \rangle|^2 \delta(\omega - E_i + E_f) \quad (33)$$

where we have integrated over all polarization angles of the emitted photon, and where the constant C and the factor ω account for the electron-photon coupling and the DOS of the photons. The fact that the core hole is annihilated during the emission process, i.e. that a rather strong perturbation is switched off, renders the emission - and the complementary absorption spectra - far more difficult to treat theoretically than the KLV Auger spectra.

The simplest, and commonly used approximation has been to neglect the effect of the core hole altogether. Both initial and final states are represented as Slater determinants, with the valence electrons described by the Bloch states of the ground state metal. For a core hole with angular momentum quantum numbers l_c, m_c , spin σ_c , and energy ϵ_c , we have $|i\rangle = a_{l_c, m_c, \sigma_c} |0\rangle$ and $|f\rangle = a_{\underline{k}, \sigma} |0\rangle$, where $\underline{k}$ denotes both band index and wave vector, σ the valence spin, and $|0\rangle$ the ground state. Averaging over degenerate initial states, i.e. over m_c and σ_c , and summing over final states, i.e. over σ and over all $\underline{k}$ within the Fermi surface ($\epsilon_{\underline{k}} \leq \epsilon_F$), Eq. (33) reduces to the usual one-particle result

$$I(\omega) = C\omega \frac{1}{2\ell_c + 1} \sum_{m_c} \sum_{\epsilon_{\underline{k}} \leq \epsilon_F} |\langle \psi_{L_c} | p | \psi_{\underline{k}} \rangle|^2 \delta(\omega + \epsilon_c - \epsilon_{\underline{k}}) \quad (34)$$

This approach takes account of bandstructure effects and has been the basis for nearly all interpretations of experimental data. While it has been rather successful, its purely ad hoc nature becomes obvious if one replaces the Bloch states of the valence electrons by impurity states obtained in the presence of the core hole. Within the one-particle approximation this should not alter the result. As is clear from our impurity calculation (cf. Fig. 3), the resulting spectra are, however, changed

drastically ⁵ . These contradictory results show that it is not possible to understand emission spectra without considering the dynamics of the process.

In 1969 Nozières and DeDominicis ²² (ND) developed a theory which goes beyond the one-particle approximation and which concentrates on the fact that the annihilation of the core hole - or its creation in absorption - switches the potential acting on the valence electrons. The asymptotic form (valid close to the edge) of their theory accounts for the edge singularities, expressing the threshold exponents in terms of the Fermi-level phase shifts of the core-hole potential. Guided by this theory and the experimental facts, the present authors were led to establish the Final State Rule ^{4, 19}, according to which both emission and absorption spectra essentially reflect the spectral properties of the final state. This rule was later confirmed by full numerical evaluations of the dynamical theory ^{5, 51, 52, 53} on realistic model systems. As such dynamical calculations including the full effect of bandstructure are yet not feasible, one may thus rely on the usual, simpler one-particle approach (Eq. (34)) to give rather realistic spectra if the one-particle wave functions used in the transition matrix elements are those corresponding to the final state. This rule then, a posteriori, provides the justification of using Eq. (34) together with the Bloch states of the ground state metal for the emission main band. Furthermore, we found that the asymptotic ND theory was approximately valid over a wider energy range than expected, and therefore we could rather

accurately account for the edge singularity by simple multiplicative, singular factors ^{52, 53}, one for each angular momentum channel.

As in the case of the Auger emission, Eq. (34) can be recast into a form only involving partial local densities of states and radial integrals. Using the commutation relations of momentum and coordinate operators, we rewrite Eq. (34) as

$$I(\omega) = C\omega^3 \frac{1}{2\ell_c+1} \sum_{m_c, v} \sum_{\underline{k}} |\langle \psi_{\underline{L}_c} | r_v | \psi_{\underline{k}} \rangle|^2 \delta(\omega + \epsilon_c - \epsilon_{\underline{k}}) \quad (35)$$

Since the core wave function vanishes outside the Wigner-Seitz sphere, we only need a description of the valence wave function within this sphere, which is given in Eq. (11). Writing the core wave function as in Eq. (9) and taking the components of the position operator to be

$$r_v = \left(\frac{4\pi}{3} \right)^{\frac{1}{2}} Y_{1,v}(\hat{r}) \cdot \underline{r} \quad (36)$$

we find

$$I(\omega) = C\omega^3 \sum_{\ell} \left\{ \sum_{\underline{k}, m} |c_{\ell, m}(\underline{k})|^2 \delta(\omega + \epsilon_c - \epsilon_{\underline{k}}) \right\} \cdot | \langle R_{\ell_c} | r | R_{\ell} \rangle |^2 \begin{pmatrix} \ell_c & 1 & \ell \\ 0 & 0 & 0 \end{pmatrix}^2 \quad (37)$$

Here, we have used the orthogonality relation (A1.4) for the Clebsh-Gordon coefficients defined in (A1.3). In (37) the term in curly brackets is just half the local partial density of states, $\mathcal{D}_{\ell}(\epsilon_c + \omega)$, of angular momentum ℓ , and we finally have

$$I(\omega) = \frac{1}{2} C\omega^3 \sum_{\ell} \mathcal{D}_{\ell}(\epsilon_c + \omega) | \langle R_{\ell_c} | r | R_{\ell} \rangle |^2 \cdot \begin{pmatrix} \ell_c & 1 & \ell \\ 0 & 0 & 0 \end{pmatrix}^2 \theta(\epsilon_F - \omega - \epsilon_c) \quad (38)$$

For $L_{2,3}$ emission in sodium, i.e. for transitions to the 2p shell, Eq. (38) reduces to

$$I(\omega) = \frac{1}{2} C\omega^3 \left[\frac{1}{3} \mathcal{D}_0(\epsilon_c + \omega) | \langle R_{2p} | r | R_0 \rangle |^2 + \frac{2}{15} \mathcal{D}_2(\epsilon_c + \omega) | \langle R_{2p} | r | R_2 \rangle |^2 \right] \theta(\epsilon_F - \omega - \epsilon_c) \quad (39)$$

while the K emission intensity (holes in the 1s shell) is

given by

$$I(\omega) = \frac{C\omega^3}{6} \mathcal{D}_1(\varepsilon_c + \omega) |<R_{1s}| r |R_1>|^2 \delta(\varepsilon_F - \omega - \varepsilon_c) \quad (40)$$

As mentioned above, we can, according to the Final State Rule 52, 53, approximately include the threshold singularity by writing

$$I(\omega) = \sum_{\ell} C_{\ell} I_{\ell}(\omega) \left(\frac{\varepsilon_F}{|\omega - \varepsilon_F|} \right)^{\alpha_{\ell}} \quad (41)$$

Here, $I_{\ell}(\omega)$ is the contribution of the ℓ -channel to the spectrum given by Eq. (38), α_{ℓ} the corresponding threshold exponent, and ε_F the Fermi energy. The constants C_{ℓ} have to be determined from the requirement that each angular momentum channel satisfy a sum rule (see Appendix 2), namely that the integrated intensity of each channel including the singular factor has to be equal to the integrated intensity of the corresponding channel of the initial state spectrum, i.e. the spectrum obtained from Eq. (38) with wave functions calculated in the presence of the core hole. Note that the frequency integrals of this sum rule should not include the photon-DOS-factor ω . Thus, the determination of the coefficients C_{ℓ} really would require solving the impurity problem. For K spectra, however, only one term ($\ell = 1$) contributes, and the magnitude of the coefficient C_1 is irrelevant as

absolute intensities are usually not measured. For $L_{2,3}$ spectra two terms in Eq. (41) contribute ($\ell = 0$ and 2), and the relative magnitudes of C_0 and C_2 could be of importance. Fortunately, in simple metals, two facts make the shape of the resulting spectra quite insensitive to the ratio C_2/C_0 : (i) the d-contribution is small in these materials (ii) the threshold exponent of the d-channel is negative, resulting in a rounding of the edge, and thus the threshold behavior is almost entirely given by the singularity of the s-channel. These points were found to be true for sodium, but were also checked for aluminium, which has the largest d-contribution (see Appendix 3).

Within the ND theory, the threshold exponent α_ℓ is determined by the Fermi-level phase shifts of the core hole potential, as is the XPS asymmetry index α :

$$\alpha_\ell = \frac{\delta_\ell}{\pi} - \alpha, \quad \alpha = \sum_{\ell} 2(2\ell+1) \left(\frac{\delta_\ell}{\pi} \right)^2$$

Due to Friedel's sum rule, the threshold exponents and the asymmetry index must satisfy compatibility relations⁵⁴. In simple metals the phase shifts for $\ell \geq 2$ are very small. Therefore, α_ℓ is directly determined by α , which is believed to be rather accurately known from experiment, $\alpha = 0.20$ ²¹, a value which agrees well with ab initio theoretical results¹⁸. α_ℓ should then be around 0.38. Using this value, we obtain an edge singularity that is not too strong compared to the experimental data published by Calcott et al.¹⁵. An accurate fit to their spectrum

actually requires an exponent as small as 0.15. The reason for this discrepancy is one of the remaining problems within the theory of x-ray edges. The present theory relies entirely on the work by Mozières and DeDominicis²², which does not take due account of the interaction between the valence electrons. We are presently investigating whether this effect could be the cause of the observed discrepancy.

In Fig. 6 we compare our result for the emission main band in sodium with the experimental data by Calcott et al.¹⁵. As discussed above, the constants C_0 and C_2 were determined from the one-core-hole calculation. For the broadened spectrum we used the same quasi-particle broadening as for the Auger spectra discussed in Sec. 4. Since the 2p-hole life-time width is small, $\Gamma \sim 10 \text{ meV}$ ¹⁵, it was negligible compared to the larger instrumental and phonon broadening. For this latter Gaussian broadening we obtained a FWHM value of 0.20 eV by fitting the Fermi edge to experiment. This value is slightly smaller than that (0.25 eV) obtained by Calcott et al. also using $\alpha_0 = 0.15$. The small discrepancy can be explained by the fact that Calcott et al. did not account for the rounded edge of the d-contribution, an approximation, which is certainly justified in sodium, where the d-channel contributes only about 2% of the total intensity. The factor ω^3 of Eq. (39) was not included, as the reported experimental spectrum already had been divided by this factor. The good agreement supports the procedure to include also the threshold behavior within

the framework of the Final State Rule.

The satellite emission spectrum arises from transitions to a doubly ionized core. In the case of $L_{2,3}$ satellite emission, the two 2p-holes give rise to three terms, namely 1D , 1S , and 3P . Calculations within the SSM and a recent analysis of experimental data by Almladh and von Barth⁵⁵ show, that only if the satellite is attributed to transitions to the 3P term, can all known data be interpreted consistently. Of course, all three terms will occur with certain probabilities in the initial excitation process creating the core holes. Due to the long life-time of the core holes, however, the excited core has time to relax to the lowest 3P state before x-ray emission takes place, which explains the absence of the higher terms in the recorded spectra.

Neglecting the spin-orbit splitting of the 3P term, there are nine degenerate initial states, some of which have to be approximated by linear combinations of Slater determinants

$$a_{2p,m,\uparrow} a_{2p,m',\uparrow} |\tilde{o}\rangle \quad (M_S=1)$$

$$\frac{1}{\sqrt{2}} \{ a_{2p,m,\uparrow} a_{2p,m',\downarrow} + a_{2p,m,\downarrow} a_{2p,m',\uparrow} \} |\tilde{o}\rangle \quad (M_S=0) \quad (42)$$

$$a_{2p,m,\downarrow} a_{2p,m',\downarrow} |\tilde{o}\rangle \quad (M_S=-1)$$

Here, the pair (m, m') takes the values $(0, 1)$, $(1, -1)$, and $(0, -1)$ corresponding to the three M_L values 1, 0, and -1. According to the Final State Rule, $|\phi^{\sim}\rangle$ should be the quasi-ground state of the metal in the presence of one core hole. The final states are of the form $a_{2p, \mu, \sigma}^{\dagger} a_{\underline{k}, \sigma'}^{\dagger} |\phi^{\sim}\rangle$. If the final states are also chosen to be spin eigenfunctions, i.e. to have definite S' and M'_S values, the matrix element of the Golden Rule (Eq. (33)) becomes

$$\begin{aligned} \langle i | P | f \rangle = & \{ \langle \psi_{2p, m'} | P | \psi_{\underline{k}} \rangle \delta_{m, \mu} - \langle \psi_{2p, m} | P | \psi_{\underline{k}} \rangle \delta_{m', \mu} \} \\ & \cdot \delta_{M_S, M'_S} \delta_{S, S'} \end{aligned} \quad (43)$$

Averaging over initial state M_S and M_L values, i.e. over the pairs (m, m') above, and summing over final state M'_S and μ values, we obtain

$$I(\omega) = C\omega \frac{2}{3} \sum_{m, \underline{k}} |\langle \psi_{2p, m} | P | \psi_{\underline{k}} \rangle|^2 \delta(\omega + \epsilon_c - \epsilon_{\underline{k}}) \quad (44)$$

which is formally identical to Eq. (34) for $\ell_c = 1$ apart from a factor 2, which is irrelevant as long as absolute intensities are not considered. Both main band and satellite spectra are thus given by the same expression, Eq. (38), the only difference being the choice of one-particle wave functions $\psi_{\underline{k}}$. As the final state of the

satellite emission contains one core hole, the relevant wave functions for this case, must according to the Final State Rule, be obtained in the presence of the core hole.

In Fig. 7 we compare our calculated satellite emission band with the experimental spectrum reported by Hansson and Arakawa⁵⁶. From SSM calculations it follows that the threshold exponent for the satellite should actually be smaller than that of the main band. Almladh and von Barth¹⁸ give a value $\alpha_0 \approx 0.20$, which is compatible with the asymmetry index $\alpha \approx 0.14$ found in the KLL spectra of sodium⁵⁷. As the theoretically predicted threshold exponent for the satellite is still larger than that needed to fit the main band, we chose to use the same threshold exponent for the theoretical satellite spectrum as for the main band. It should be noted, that due to strong broadening effects the satellite spectrum is quite insensitive to the choice of threshold exponent, and no attempt was made to extract an exponent by fitting to experiment. Apart from the same quasi-particle broadening as in the main band, we here used a Gaussian broadening whose FWHM value of 0.58 again was obtained by fitting to the experimental Fermi edge. This Gaussian broadening accounts for not only instrumental and phonon broadening, but also simulates the shorter life of the doubly ionized core and unresolved structure due to spin-orbit splitting (~ 0.2 eV⁵⁸) of the doubly excited core.

We performed the calculations discussed above also for lithium. Here, the core holes are located in the 1s

shell. Due to the dipole selection rules, (cf. Eq. (40)), both main band and satellite emission spectra reflect the partial local DOS of p character. The effect of a core hole turned out to be very similar to that found in sodium as is seen in Fig. 8. The analysis of our calculation shows that the structure near the Fermi level, both in the local DOS and in the corresponding emission intensity, is largely due to the interaction between the impurities on the superlattice. The effect is much stronger than in sodium which is a consequence of the stronger bandstructure effects just above the Fermi energy. The effect is, however, small enough not to affect our main conclusion, namely that the shape of the x-ray spectra is independent of the core hole. The spectral distribution of s electrons is again strongly enhanced near the bottom of the band, while the local p state density is approximately doubled, yet retains its shape almost unchanged. The one-particle emission spectra calculated with wave functions obtained in the presence of or without a core hole thus closely agree (Fig. 9), i.e. the calculation predicts the satellite to have the same shape as the main band, if we disregard all effects due to different broadenings, and this prediction is confirmed by experiment⁵⁹. We have here made no attempt to use our calculated intensities together with the Final State Rule in order to make a detailed comparison with the experimental K emission main band and satellite spectra. Lithium is a case where the emission spectrum is known⁶⁰ to be strongly influenced by effects due to incomplete relaxation of phonons. The anomalous shape of the lithium K edge is due to these

effects⁶¹. In Ref. 60 the spectrum constructed from our no-core-hole intensity, but also including the incomplete relaxation effects, is compared with experiment¹⁴. The detailed agreement is indeed gratifying.

In general, we thus find the satellite K-emission spectra in simple metals to be very similar to the main band, whereas the satellite $L_{2,3}$ emission spectra show a peak near the bottom of the band, which is absent from the main band spectrum. This is then simply a reflection of the fact that what we see in emission experiments is essentially the local DOS of the final state, and while p electrons are only rather uniformly enhanced, s electrons are strongly distorted by a core hole.

We end this section with a few comments on the immediate implications of our numerical results and of the Final State Rule on the spectra of simple metal alloys. Some aspects of these spectra have previously been discussed by Jacobs⁶² and Inglesfield⁶³. According to the equivalent core approximation¹⁸, one would expect the local electronic structure around a core-ionized atom in a ground state matrix to be quite similar to that around an impurity atom whose valence is one unit greater than that of the host metal. As emission spectra probe the spectral properties of the final state, the emission spectra from such an impurity in a dilute alloy should show features similar to the satellite emission spectra of the host metal. Indeed, this expectation is confirmed by the emission spectra of several AlMg alloys measured by

Neddermeyer¹². For the dilute systems $\text{Al}_5\text{Mg}_{95}$ and $\text{Al}_{10}\text{Mg}_{90}$ the reported K emission spectra are nearly identical in shape for both constituents, in analogy to the agreement in shape of the lithium emission main band and the corresponding satellite. The $\text{L}_{2,3}$ emission spectra, on the other hand, differ markedly. While the Mg $\text{L}_{2,3}$ emission is the same as in pure Mg, the Al $\text{L}_{2,3}$ emission is much broader and is dominated by a pronounced peak near the bottom of the common valence band. In analogy to the sodium satellite spectrum we expect a theoretical Al $\text{L}_{2,3}$ emission spectrum to exhibit a sharp peak near the bottom of the band, the broadening of which will yield a noticeably broader spectrum. As the relative concentration of Al increases, also the width of the valence band increases, varying from the width of pure Mg to that of pure Al. From our calculations we expect the peak in the local partial s DOS of Al sites to grow broader due to the increased interaction between neighboring "impurities", and this is clearly seen in the experimental spectra. The shapes of the p-state densities of both Al and Mg should, however, be much less affected. As a matter of fact, the two K emission spectra remain nearly identical at all compositions.

The same trends are also observed in the recent measurements on LiMg and LiAl alloys by Tagle et al.¹⁶. For the LiMg alloys one finds that as the concentration of Mg atoms decreases, the Mg $\text{L}_{2,3}$ band narrows and again exhibits an increasingly pronounced peak near the bottom of the band. The position of this peak agrees well with

that of the s-peak seen in the local DOS of a core-hole atom in lithium (Fig. 8). Aluminium in lithium corresponds to the case of two core holes on a sodium atom, for which we expect a bound state at infinite dilution and, as seen in Fig. 2c, a strong distortion at finite concentrations. Calculations for clusters containing one excited atom with two 2p holes and one or three ground state atoms show, that the s electrons at the excited atom are essentially confined to the lower half of the band, which also is apparent from the experimental Al $L_{2,3}$ spectra. We thus find that the general trends of alloy spectra can be explained on the basis of the present calculations and the Final State Rule. Any more detailed interpretation will, of course, have to take into account the actual atomic species in their proper crystal structure.

6. Conclusions.

In the present paper we have discussed the effect of the core hole on the shape of several spectra in simple metals, namely KLV Auger spectra, soft x-ray emission (SXE) and absorption (SXA) spectra and SXE satellite spectra. From calculations of particular spectra for specific systems, i.e. KL_1V and $KL_{2,3}V$ Auger in sodium, $L_{2,3}$ main band and satellite emission in sodium, K main band and satellite emission in lithium, we have identified the dominant physical effects, which in turn has allowed us to make predictions for similar spectra in other simple metals and their alloys. The methods and detailed results discussed in the present paper have been the basis for earlier shorter notes and conference contributions by the authors^{4, 5, 20} and for papers by other workers^{19, 51, 3.}

From a many-body point of view, the theoretical description of the KLV Auger spectra is less demanding than that of SXE and SXA. Starting from the full Golden Rule expression for the rate of Auger transitions from a many-body state with a hole in the K-shell to states with a hole in the L-shell, we discussed the approximations which led to an effective one-particle description of the process. These approximations involve the neglect of several many-body effects such as incomplete relaxation, the interaction between the Auger electron and the solid left behind, surface scattering of the escaping Auger

electron, and the detailed interaction between the valence electrons of the solid. The latter interaction only enters into our description via an energy dependent quasi-particle broadening of the resulting Auger spectrum. This broadening is zero at the Fermi edge and increases quadratically in energy towards the bottom of the band with a curvature that we determined by fitting to experiment. The life time broadening of the K and L core levels is a second many-body effect that we accounted for by convoluting the final Auger spectra with Lorentzians, whose widths are determined from XPS experiments ²¹. The most important "many-body" effect, however, is to be attributed to the core holes, which are present in the initial (K) and the final (L) states of the Auger process. These holes have a strong influence on the effective one-particle description of the Auger spectra, and the necessity for incorporating their effect follows naturally from our analysis of the full expression describing the process. One can, however, consider the two different core holes to have the same effect on the valence electrons (the equivalent core approximation), and thus, one can neglect all dynamics associated with the very small change in potential from one core hole to the other.

The presence of a static core hole makes our effective one-particle description considerably more demanding than a bandstructure calculation, in that the local state densities entering this description must reflect the self-consistent valence charge screening the hole. Into this description we have then introduced

approximations such as treating the wave function of the outgoing Auger electron as a free spherical wave outside the central cell, obtaining the self-consistently screened core-hole potential and the local partial state densities from repeated cluster calculations with a limited number (16) of atoms and using a limited set of basis functions for solving the cluster problem. All these approximations are discussed at length in the paper and it is concluded that they may introduce errors of a magnitude comparable to the experimental uncertainties. Our calculated KL_1V and $KL_{2,3}V$ spectra for sodium agree quite well with the experimental spectra by Barrie and Street ² and by Lässer and Fuggle ³. This agreement supports our main conclusion concerning the origin of the "mystery" peaks observed at the low energy end of the experimental spectra. The KLV spectra are essentially given by a weighted sum of the s and p partial state densities of the valence electrons (Eq. (19) and (20)). The weights, which are determined not only by Clebsh-Gordon coefficients but also by radial matrix elements, are different for KL_1V and $KL_{2,3}V$, which explains the different shapes of these spectra. As these weights vary slowly over the width of the band, the strong structure exhibited by both spectra near the bottom of the band cannot be a matrix element effect, it rather reflects an intrinsic property of the local state densities. Indeed, compared to the ground state solid, the presence of the core hole distorts the local partial state density of s character strongly, shifting oscillator strength towards lower energies. Incorporating this essential effect, we are able to give the first interpretation of

the "mystery" peaks. These peaks are present in all KLV spectra of simple metals, and we conclude that they all have a common origin in the core hole strongly affecting the valence electrons. This effect will influence the CCV spectra in other materials such as semiconductors³ and probably also transition metals.

Given the strong static effect of the core hole on KLV Auger spectra, it seems natural to expect the hole to have an important influence also on SXE and SXA spectra. It is, however, well known that the SXE spectra of simple metals are rather well reproduced by a simple one-particle theory in which the x-ray transition is considered to take place between a core state and a valence Bloch state of the ground state solid. If the resulting spectrum is also multiplied with a power-law singularity and broadened, the agreement between theory and experiment becomes almost perfect^{66, 15}. Thus, the presence of the core hole in the initial state of the emission process has very little effect on the shape of the spectrum except for the threshold singularity. X-ray absorption, on the other hand, probes the density of unoccupied valence states. Our calculations show, that in the simple metals the shape of these densities is much less affected by the presence of the screened hole. Thus, it may be difficult, in some cases, to detect a core-hole effect on the basis of experiment. It is, however, well known in atomic physics⁶⁴ that the many-body perturbation expansion for the photoabsorption cross section converges much more rapidly if one chooses one-particle basis functions

obtained in the fully relaxed potential including the hole left behind. On the basis of these observations the present authors postulated the Final State Rule⁴, according to which very accurate x-ray emission and absorption spectra in simple metals can be obtained from simple one-particle theory provided the transition matrix elements are calculated from one-particle wave functions obtained in the potential of the final state, i.e. including the hole in absorption but not in emission. The Final State Rule also states⁵² that even the threshold region can be accurately described by multiplying the one-particle transition density of states of each angular momentum channel by power-law singularities with appropriate exponents. Further support for the Final State Rule was later obtained by the authors^{5, 52} and by Mahan⁵¹ from direct numerical evaluations of the theory by Nozières and DeDominicis²². In fact, to date, there are no known systems for which the numerical solution to the ND theory does not obey the Final State Rule. The ND theory does not account for the interaction between the valence electrons, but it incorporates the important dynamics of the x-ray transition, i.e. the fact that the core hole potential is switched off (on) in the emission (absorption) process. The theory also provides an analytical formula for the threshold exponents in terms of the Fermi-level phase shifts of the core-hole potential. In this paper we have used the Final State Rule together with the required Bloch functions of the ground state crystal to calculate the emission spectra of sodium ($L_{2,3}$) and lithium (K). Our theoretical spectrum for sodium also

includes Lorentzian broadening to account for the life time of the core hole, energy dependent Lorentzian broadening to account for the life times of the valence holes, and Gaussian broadening to account for the phonon coupling and for the limited instrumental resolution. The good agreement with experiment obtained for sodium strongly supports the Final State Rule. The agreement is good also for lithium, provided the incomplete relaxation of phonons is accounted for ⁶⁰. Perhaps the most exciting piece of information revealed by the sodium spectrum ¹⁵ is that the exponent ($\alpha_o = 0.15$) of the singular factor needed in the s-channel in order to fit the theoretical spectra to experiment is quite different from that ($\alpha_o = 0.38$) predicted by ab initio calculations or by XPS experiments on the basis of ND theory. The discrepancy is very large and suggests that the physics of the x-ray edges is not fully understood.

Encouraged by the success of the Final State Rule in describing the main band emission spectra in sodium and lithium and numerous other emission and absorption spectra in model systems ^{52, 53}, we used it to obtain the corresponding satellite spectra. These spectra arise when one of two initially created holes in the same shell is filled by a valence electron and the final states of such a process thus have a core hole. Therefore, the relevant one-particle orbitals are those of the impurity problem and these we had obtained from our cluster calculations. For $L_{2,3}$ satellite emission the transition matrix elements differ from the main band in that the initial two-hole

states have to be coupled to form eigenfunctions of total angular momentum and spin (3P). The analysis leads, however, to a similar expression as that for the main band. For our satellite spectrum of sodium we used the same threshold exponent and the same quasi-particle broadening as for the main band, but the overall broadening is larger to account for the shorter life time of the two-hole state and for unresolved structure due to spin-orbit splitting. The agreement with experiment is again gratifying and supports the Final State Rule. Our theory gives the first correct interpretation of the strong structure seen near the bottom of the satellite emission band by attributing this effect to the presence of a core hole in the final state. The same structure is seen also in the $L_{2,3}$ satellite emission spectra in Mg and Al and we conclude that the hole is responsible also for these structures. The K emission, on the other hand, probes the local p density of states whose shape, according to our calculation, is almost unaffected by the core-hole potential. Therefore, the main band and the satellite spectrum have the same appearance in lithium.

The ideas and the calculations of the present paper also have immediate implications for the emission spectra of simple metal alloys. For instance, in alloys consisting of magnesium and a rather low concentration of aluminium, an Al atom can be considered as an impurity with an extra proton whose effect on the valence electrons is very similar to that of a Mg atom with a core hole (the equivalent core approximation). Therefore, the initial

state of the Al $L_{2,3}$ emission main band can be thought of as having two core holes, and the final state as having one. Consequently, we would expect this emission spectrum to be very similar in shape to the magnesium $L_{2,3}$ satellite spectrum and this is indeed the case. The shapes of the K spectra, on the other hand, agree rather closely for both constituents in analogy to K emission spectra in lithium. Thus, also alloy spectra may show the strong static effect of a core hole, while its dynamic effect is rather accurately accounted for by the Final State Rule.

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7. Appendix 1.

In this appendix we evaluate the square

$$|M_{KLV}(A)|^2 = |\langle A, K | v | V, L \rangle|^2 + |\langle A, K | v | L, V \rangle|^2 - 2 \operatorname{Re} \left[\langle A, K | v | V, L \rangle^* \langle A, K | v | L, V \rangle \right] \quad (A1.1)$$

of the Auger matrix element $M_{KLV}(A)$ (Eq.(5)), averaged over degenerate initial states and summed over degenerate final states. We make use of the expansion of the Coulomb interaction $v(\underline{r} - \underline{r}')$ in terms of the spherical harmonics $Y_L(\hat{r})$

$$v(\underline{r} - \underline{r}') = \sum_L \frac{4\pi}{2\ell+1} U_\ell(r, r') Y_L(\hat{r}) Y_L^*(\hat{r}') \quad (A1.2)$$

where $U_\ell(r, r') = r_{<}^\ell / r_{>^{\ell+1}}$, and $r_{<}$ and $r_{>}$ are the lesser and the larger of r and r' . The label L is short for (l, m) . The matrix elements contain the Clebsch-Gordon coefficients $K(L_1, L_2, L_3)$ that are defined by

$$K(L_1, L_2, L_3) = \int Y_{L_1}(\hat{r}) Y_{L_2}(\hat{r}) Y_{L_3}(\hat{r}) d\Omega \quad (A1.3)$$

and which satisfy the orthogonality relation

$$\sum_{m_1, m_2} K(L_1, L_2, L_3) \cdot K(L_1, L_2, L_3') = \frac{1}{4\pi} (2\ell_1+1)(2\ell_2+1) \cdot \begin{pmatrix} \ell_1 & \ell_2 & \ell_3 \\ 0 & 0 & 0 \end{pmatrix}^2 \delta_{L_3, L_3'} \quad (A1.4)$$

Here, $\begin{pmatrix} \ell_1 & \ell_2 & \ell_3 \\ m_1 & m_2 & m_3 \end{pmatrix}$ is an ordinary "3j" symbol⁶⁵.

Applying Eq. (A1.4), the first term in Eq. (A1.1) leads to

$$\sum_{\sigma_A, m_A} \sum_{\sigma_L, m_L} |\langle A, K | v | V, L \rangle|_{av}^2 =$$

$$\frac{1}{2} \mathcal{D}_{\ell_A}(\epsilon_A) \sum_{\ell} \sum_{L_V} |c_{L_V}(k_V)|^2 R_{\ell}^2(A, K; \ell_V, L) \quad (A1.5)$$

$$\cdot \frac{2\ell_L + 1}{2\ell + 1} \begin{pmatrix} \ell_A & \ell_V & \ell \\ 0 & 0 & 0 \end{pmatrix}^2 \begin{pmatrix} \ell_K & \ell_L & \ell \\ 0 & 0 & 0 \end{pmatrix}^2$$

where σ and m designate spin and magnetic quantum numbers of the respective electrons. The subscript av indicates that the averaging over initial states $\left[\frac{1}{2} (2\ell_K + 1)^{-1} \sum_{\sigma_K, m_K} \right]$ has been carried out. The radial integral $R_{\ell}(a, b, c, d)$; is defined by

$$R_{\ell}(a, b, c, d) =$$

$$\int_0^{\infty} \int_0^{\infty} R_a(r) R_b(r') U_{\ell}(r, r') R_c(r) R_d(r') r^2 r'^2 dr dr' \quad (A1.6)$$

Similarly, we find for the contribution of the second term in Eq. (A1.1)

$$\begin{aligned}
& \sum_{\sigma_A, m_A} \sum_{\sigma_L, m_L} |\langle A, K | v | L, V \rangle|_{av}^2 = \\
& \frac{1}{2} \mathcal{D}_{\ell_A}(\epsilon_A) \sum_{\ell} \sum_{L_V} |c_{L_V}(\underline{k}_V)|^2 R_{\ell}^2(A, K; L, \ell_V) \\
& \cdot \frac{2\ell_L+1}{2\ell+1} \begin{pmatrix} \ell_K & \ell_V & \ell \\ 0 & 0 & 0 \end{pmatrix}^2 \begin{pmatrix} \ell_L & \ell_A & \ell \\ 0 & 0 & 0 \end{pmatrix}^2
\end{aligned} \tag{A1.7}$$

We can in general, for arbitrary angular momenta of the two core holes, not use the orthogonality relation of the Clebsh-Gordon coefficients (A1.4) to simplify the cross-term in Eq. (A1.1), which then looks much more complicated. We find

$$\begin{aligned}
& \langle A, K | v | V, L \rangle^* \langle A, K | v | L, V \rangle = \delta_{\sigma_A, \sigma_V} \delta_{\sigma_K, \sigma_L} \delta_{\sigma_A, \sigma_L} \delta_{\sigma_K, \sigma_V} \\
& \cdot \frac{1}{2\ell_A+1} \mathcal{D}_{\ell_A}(\epsilon_A) \sum_{L_1, L_2} \sum_{L_V, L'_V} c_{L_V}^*(\underline{k}_V) c_{L'_V}(\underline{k}_V) \\
& \cdot R_{\ell_1}(A, K; \ell_V, L) R_{\ell_2}(A, K; L, \ell'_V) \frac{4}{2\ell_1+1} \frac{4}{2\ell_2+1} \\
& \cdot K(L_V, L_A, L_1)^* K(L_K, L_L, L_1)^* K(L_L, L_A, L_2)^* K(L_K, L'_V, L_2)^*
\end{aligned} \tag{A1.8}$$

where $K(L_1, L_2, L_3)^*$ implies replacing m_1 by $-m_1$ in $K(L_1, L_2, L_3)$ and multiplying by $(-1)^{m_1}$. It may seem as if this cross term will depend on the details of the valence wave function at each $\underline{k}$ -point in the Brillouin zone, which would mean that the $\underline{k}$ -summation does not just yield partial-density-of-states-factors as it will for the terms

(A1.5) and (A1.7). One can, however, show that the product of Clebsh-Gordon coefficients will give rise to a factor δ_{L_V, L_V} times a "6j" symbol⁶⁵ when the proper summations over m_A , m_L , and m_K (and m_1 , m_2) are performed. Thus the coefficients c_{L_V} will only enter the final expression in the form $\sum_{m_V} |c_{L_V}|^2$ and also the cross term will then only contain the partial valence densities of states. Still, this term will appear to be relatively complicated but it simplifies enormously if we take into account the spherical symmetry of an electron in the K shell ($\ell_K = 0$). Then $K(L_K^*, L_A, L_B) = \delta_{L_A, L_B} / \sqrt{4\pi}$ and we get

$$\begin{aligned} \sum_{\sigma_A, m_A} \sum_{\sigma_L, m_L} |\langle A, K | v | V, L \rangle^* \langle A, K | v | L, V \rangle|_{av} = \\ \frac{1}{4} \vartheta_{\ell_A}(\epsilon_A) \sum_{L_V} |c_{L_V}(K_V)|^2 R_{\ell_L}(A, K; \ell_V, L) \\ \cdot R_{\ell_V}(A, K; L, \ell_V) \frac{1}{2\ell_V+1} \begin{pmatrix} \ell_A & \ell_L & \ell_V \\ 0 & 0 & 0 \end{pmatrix}^2 \end{aligned} \quad (A1.9)$$

If we introduce $\ell_K = 0$ also in Eqs. (A1.5) and (A1.7) we obtain

$$\begin{aligned} \sum_{\sigma_A, m_A} \sum_{\sigma_L, m_L} |M_{KL V}(A)|_{av}^2 = \\ \frac{1}{2} \vartheta_{\ell_A}(\epsilon_A) \sum_{L_V} |c_{L_V}(K_V)|^2 (2\ell_L+1) \begin{pmatrix} \ell_A & \ell_V & \ell_L \\ 0 & 0 & 0 \end{pmatrix}^2 \\ \cdot (\bar{R}_{\ell_L}^2(A, K; \ell_V, L) + \bar{R}_{\ell_V}^2(A, K; L, \ell_V) \\ - \bar{R}_{\ell_L}(A, K; \ell_V, L) \cdot \bar{R}_{\ell_V}(A, K; L, \ell_V)) \end{aligned} \quad (A1.10)$$

where the barred integral $\bar{R}_\ell$ is the unbarred integral R_ℓ divided by $2\ell+1$, and where we have used the fact that⁶⁵

$$\begin{pmatrix} 0 & \ell & \ell^- \\ 0 & 0 & 0 \end{pmatrix}^2 = \frac{\delta_{\ell\ell^-}}{2\ell+1} \quad (\text{A1.11})$$

Averaging over initial states (subscript av) in the case of an initial K-hole is simply an average over the K-hole spin, $\frac{1}{2} \sum_{\sigma_K}$. Due to the chosen normalization of the Auger wave function (Eq. (14)), we have the simple rule

$$\sum_A \equiv \sum_{\sigma_A, L_A} \int d\varepsilon_A. \quad \text{Similarly, we have } \sum_L \equiv \sum_{\sigma_L, m_L} \text{ and}$$

$\sum_V \equiv \sum_{\sigma_V, \underline{k}_V}$, where an extended zone scheme is used for the $\underline{k}$ -vectors in order to avoid band indices. Thus, we can write

$$\begin{aligned} \sum_{A,L,V} |M_{KLV}(A)|_{av}^2 \delta(\omega - \varepsilon_A) \delta(\omega - \varepsilon_V(\underline{k}_V)) = \\ \frac{1}{2} \sum_{\ell_A, \ell_V} \mathcal{D}_{\ell_A}(\omega) \mathcal{D}_{\ell_V}(\omega^-) (2\ell_L + 1) \begin{pmatrix} \ell_A & \ell_V & \ell_L \\ 0 & 0 & 0 \end{pmatrix}^2 \\ \cdot \left(\bar{R}_{\ell_L}^2(A, K; \ell_V, L) + \bar{R}_{\ell_V}^2(A, K; L, \ell_V) \right. \\ \left. - \bar{R}_{\ell_L}(A, K; \ell_V, L) \cdot \bar{R}_{\ell_V}(A, K; L, \ell_V) \right) \end{aligned} \quad (\text{A1.12})$$

where we have introduced the local partial density of valence states, $\mathcal{D}_\ell(\omega)$, defined in Eq. (16). The partial valence DOS, $\mathcal{D}_{\ell_V}(\omega)$, is to be evaluated at energies near ϵ_F , while the partial DOS for the Auger electrons, $\mathcal{D}_{\ell_A}(\omega)$, is needed at rather high energies, $\omega \sim 1$ keV, which is one of the motivations for the spherical approximation used to obtain $\mathcal{D}_{\ell_A}(\omega)$.

8. Appendix 2.

The dynamical transition density of states (TDOS) is defined by

$$TD^{ND}(\omega) = \sum_f |\langle f | \underline{T} | i \rangle|^2 \delta(E_i - E_f - \omega) \quad (A2.1)$$

in terms of which the emission spectrum, Eq. (33), is given by $I(\omega) = C\omega \cdot TD^{ND}(\omega)$. Writing the transition operator $\underline{T}$, responsible for transitions involving the core state c , as

$$\underline{T} = \sum_V \underline{p}_{cV} a_V a_c^\dagger \quad (A2.2)$$

with $\underline{p}_{cV} = \langle c | \underline{p} | V \rangle$ and where the sum extends over all valence states V , we find

$$\int TD^{ND}(\omega) d\omega = \sum_{VV'} \underline{p}_{cV}^* \underline{p}_{cV'} \langle i | a_c a_V^\dagger a_{V'} a_c^\dagger | i \rangle. \quad (A2.3)$$

where we have used the completeness of the final states $|f\rangle$. Within ND theory both $|i\rangle$ and $|f\rangle$ are non-interacting many-electron states and if we take the one-particle states V to be those of the initial state with a core hole, the matrix element of Eq. (A2.3) yields a $\delta_{VV'}$ factor and restricts the sum to occupied one-particle states. We then have

$$\int \text{TD}^{\text{ND}}(\omega) d\omega = \sum_V^{\text{occ}} |\underline{p}_{\text{CV}}|^2 = \int \text{TD}^{\text{I}}(\omega) d\omega \quad (\text{A2.4})$$

Thus, the integrated dynamical TDOS is equal to the integrated TDOS of the initial state, $\text{TD}^{\text{I}}(\omega)$.

For cubic systems, it is easily seen that this sum rule also holds true for each of the angular momentum channels considered here. Choosing all final states $|f\rangle$ as basis functions $|f_\alpha\rangle$ to the irreducible representations Γ_α of the point group O_h , we can decompose $\text{TD}^{\text{ND}}(\omega)$ into α -channels:

$$\begin{aligned} \text{TD}^{\text{ND}}(\omega) &= \sum_{\alpha} \sum_{f_{\alpha}} |\langle f_{\alpha} | \underline{T} | i \rangle|^2 \delta(E_i - E_f - \omega) \\ &= \sum_{\alpha} \text{TD}_{\alpha}^{\text{ND}}(\omega) \end{aligned} \quad (\text{A2.5})$$

For the integrated dynamical TDOS of the α -channel we then have

$$\int \text{TD}_{\alpha}^{\text{ND}}(\omega) d\omega = \sum_{V,V'} \underline{p}_{\text{CV}}^* \underline{p}_{\text{CV}'} \langle i | a_{\text{C}} a_{\text{V}}^{\dagger} | f_{\alpha} \rangle \langle f_{\alpha} | a_{\text{V}'} a_{\text{C}}^{\dagger} | i \rangle \quad (\text{A2.6})$$

We write the initial state as $|i\rangle = a_{\text{C}} |N^{\sim}\rangle$, where $|N^{\sim}\rangle$ describes a filled, spherically symmetric core and N valence electrons in their quasi-ground state in the presence of a core-hole potential. Assuming the core hole

potential to have cubic symmetry, the state $|\tilde{N}\rangle = a_c^\dagger |i\rangle$ belongs to the identical representation Γ_1 , and the symmetries of the states $a_{Vc}^\dagger |i\rangle$ are determined by the symmetries of the one-particle states V . As states of different symmetry are orthogonal, the sum over V and V' may be restricted to states of α symmetry. Thus the sum over final states $|f_\alpha\rangle$ becomes the resolution of unity in this subspace, and again taking the states V to be those of the initial state, we finally have

$$\int TD_\alpha^{ND}(\omega) d\omega = \sum_{V(\Gamma_\alpha)}^{occ} |\underline{p}_{cV}|^2 = \int TD_\alpha^I(\omega) d\omega \quad (A2.7)$$

where $TD_\alpha^I(\omega)$ is the TDOS of the initial state in the channel α .

When expanding the one-particle valence states of symmetry α in spherical harmonics in the central atomic sphere, the representation Γ_α will determine which angular momenta may occur in the expansion. For K and L emission spectra we are only interested in valence states with $l \leq 2$, and for cubic systems s and p contributions correspond uniquely to two different irreducible representations Γ_1 and Γ_{15} , while the d contribution corresponds to two other irreducible representations Γ_{12} and Γ_{25^-} . Thus, defining the s, p, and d TDOS as $TD_1^{ND}(\omega)$, $TD_{15}^{ND}(\omega)$ and $TD_{12}^{ND}(\omega) + TD_{25^-}^{ND}(\omega)$, respectively, we see that the sum rule is obeyed for each angular momentum channel.

9. Appendix 3.

To estimate the relative importance of the s and d contributions (C_2/C_0) in the Al $L_{2,3}$ emission spectrum, we treat Al in the free electron approximation. We take the partial transition DOS of the final state, $TD_\ell^F(\omega)$, to be given by the free-electron partial DOS which is scaled to fulfill $TD_2^F(\epsilon_F)/TD_0^F(\epsilon_F) = 0.52$, a value given by the SSM¹⁸. Choosing the set of Fermi level phase shifts to be $\delta_0 = 0.46$, $\delta_1 = 0.34$ and $\delta_2 = .02$ ⁶⁶, we can then use Friedel's sum rule to obtain a reasonable estimate of the integrated partial transition DOS of the initial state, $\int TD_\ell^I(\omega) d\omega$, for $\ell = 0, 1$, and 2. From the phase shifts we also have $\alpha_0 = 0.179$ and $\alpha_2 = -0.101$. Writing the dynamical transition DOS for each channel as prescribed by the Final State Rule (Eq. (41)),

$$TD_\ell^{ND}(\omega) = C_\ell \cdot TD_\ell^F(\omega) \cdot \left(\frac{\epsilon_F}{|\omega - \epsilon_F|} \right)^{\alpha_\ell} \quad (A3.1)$$

and using the sum rule (A2.7), we finally obtain $C_0 = 1.02$ and $C_2 = 1.45$.

The total d-contribution is of the order of 10%, and as long as bandstructure effects do not add any significant structure, the d-contribution can essentially

only affect the shape of the spectrum near the Fermi edge. To estimate its effect on the edge singularity, we constructed a broadened spectrum from the above parameters. We then tried to retrieve the parameters by fitting this spectrum with a broadened version of Eq. (A3.1), using the threshold exponents and the broadening as fitting parameters and arbitrarily forcing C_0 and C_2 to be equal. In this way, we obtained e.g. $\alpha_0 = 0.169$, which is indeed very close to the input value. We thus conclude (see also Ref. 66) that even in Al, which has the largest d-contribution of the simple metals, the emission spectrum is quite insensitive to the ratio of C_2/C_0 .

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Figure captions.

Figure 1. The Brillouin zone of a bcc lattice (sodium, lithium) together with the smaller cubic Brillouin zone corresponding to the 16-atom cubic supercell.

Figure 2. The energy bands in the (100)-direction obtained from the 16-atom supercell calculation for the three cases: the "impurity", which is surrounded by 15 ground state sodium atoms is a ground state atom (a), a sodium atom with a 2p core hole (b), and a sodium atom with two 2p core holes (c).

Figure 3. The angular momentum decomposed density of states for sodium, multiplied by a factor 2 (left), and the local DOS for a sodium atom with a core hole in sodium (right). Note the strong distortion of the local s-DOS due to the presence of the core hole, whereas the shape of the local p-DOS remains almost unchanged.

Figure 4. Theoretical and experimental (dotted curve, Ref. 2) KL_1 Auger spectrum for sodium. The solid curve is broadened as discussed in the text. Note that the unbroadened (dashed) spectrum is shifted upwards for clarity.

Figure 5. Theoretical and experimental (dotted curve, Ref. 2) $KL_{2,3}V$ Auger spectrum for sodium. The solid curve is broadened as discussed in the text. Note that the unbroadened (dashed) spectrum is shifted upwards for clarity.

Figure 6. Theoretical and experimental (dotted curve, Ref. 15) $L_{2,3}$ main band emission spectrum of sodium. The solid curve is broadened as discussed in the text. Note that the unbroadened (dashed) spectrum is shifted upwards for clarity.

Figure 7. Theoretical and experimental (dotted curve, Ref. 56) $L_{2,3}$ emission satellite spectrum of sodium. The solid curve is broadened as discussed in the text. Note that the unbroadened (dashed) spectrum is shifted upwards for clarity.

Figure 8. Local density of states for a ground state atom in lithium multiplied by a factor 2 (left), and the local DOS for an atom with a core hole in lithium (right). Note the similarity to the corresponding curves for sodium in Fig. 3.

Figure 9. Comparison of the unbroadened one-particle K-emission spectra for lithium taking the $1s$ core hole into account (solid line) or not (dashed line). After broadening the resulting spectra will be nearly indistinguishable.

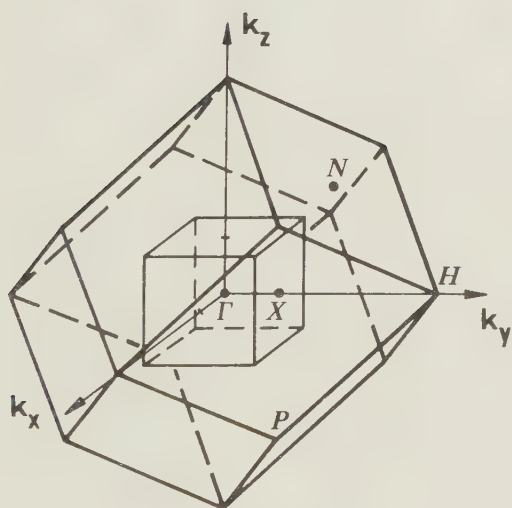


FIGURE 1

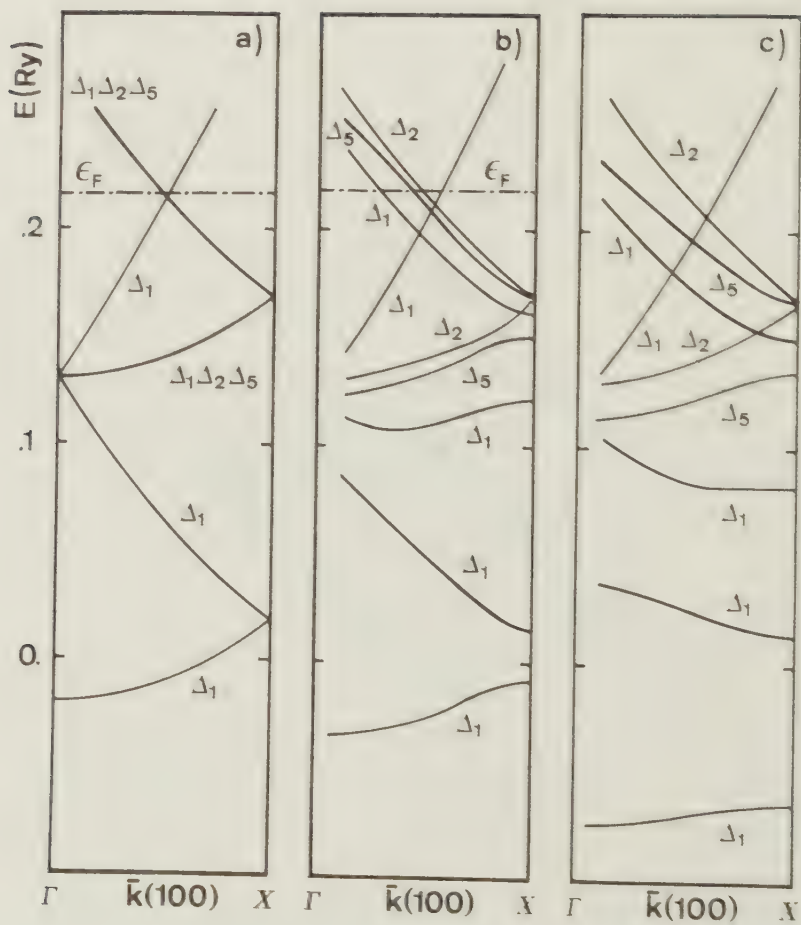


FIGURE 2

FIGURE 3

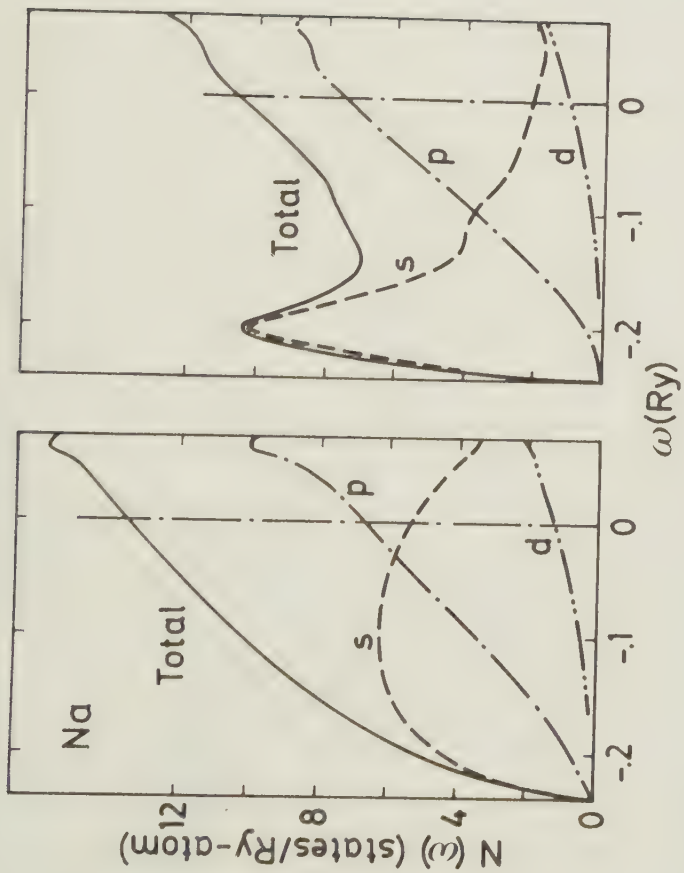


FIGURE 4

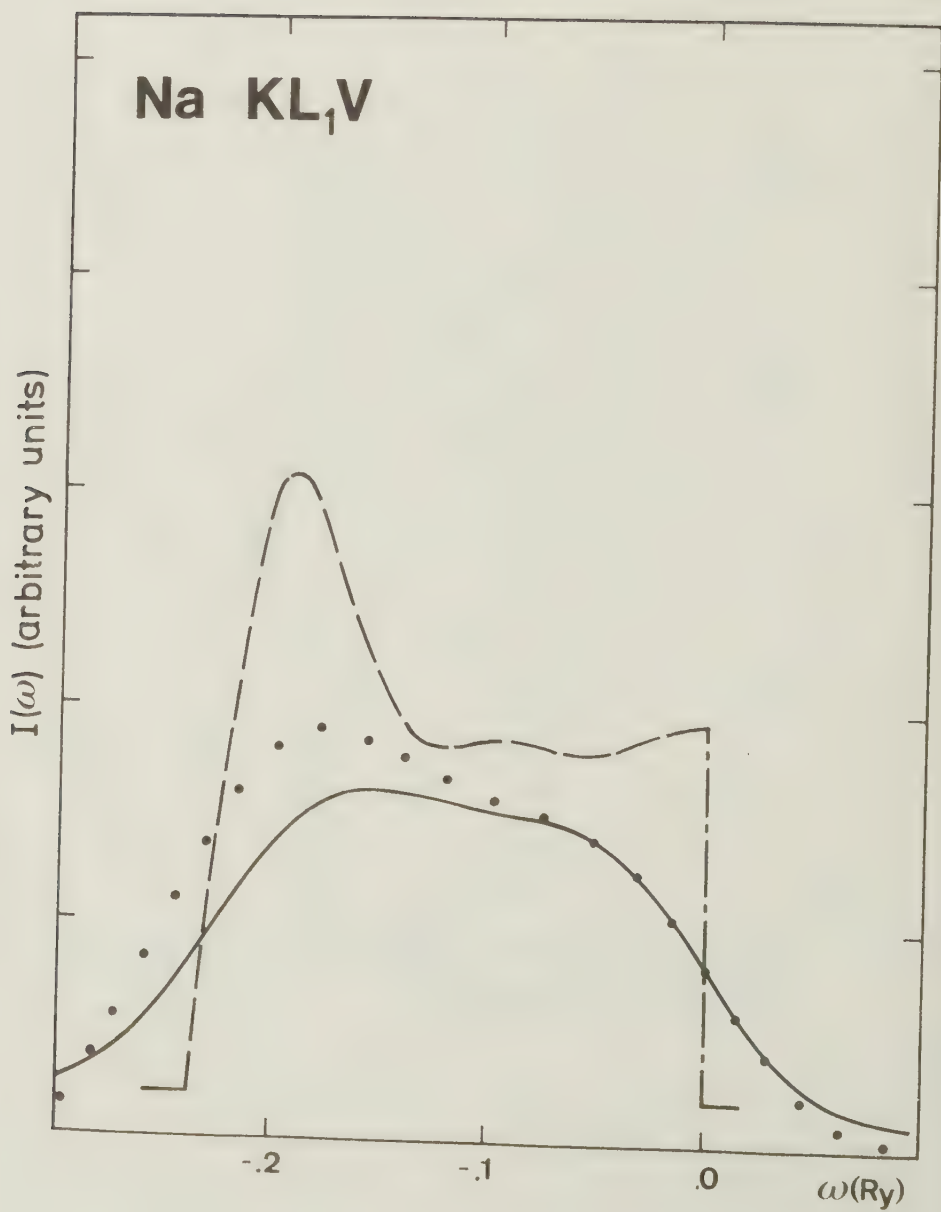


FIGURE 5

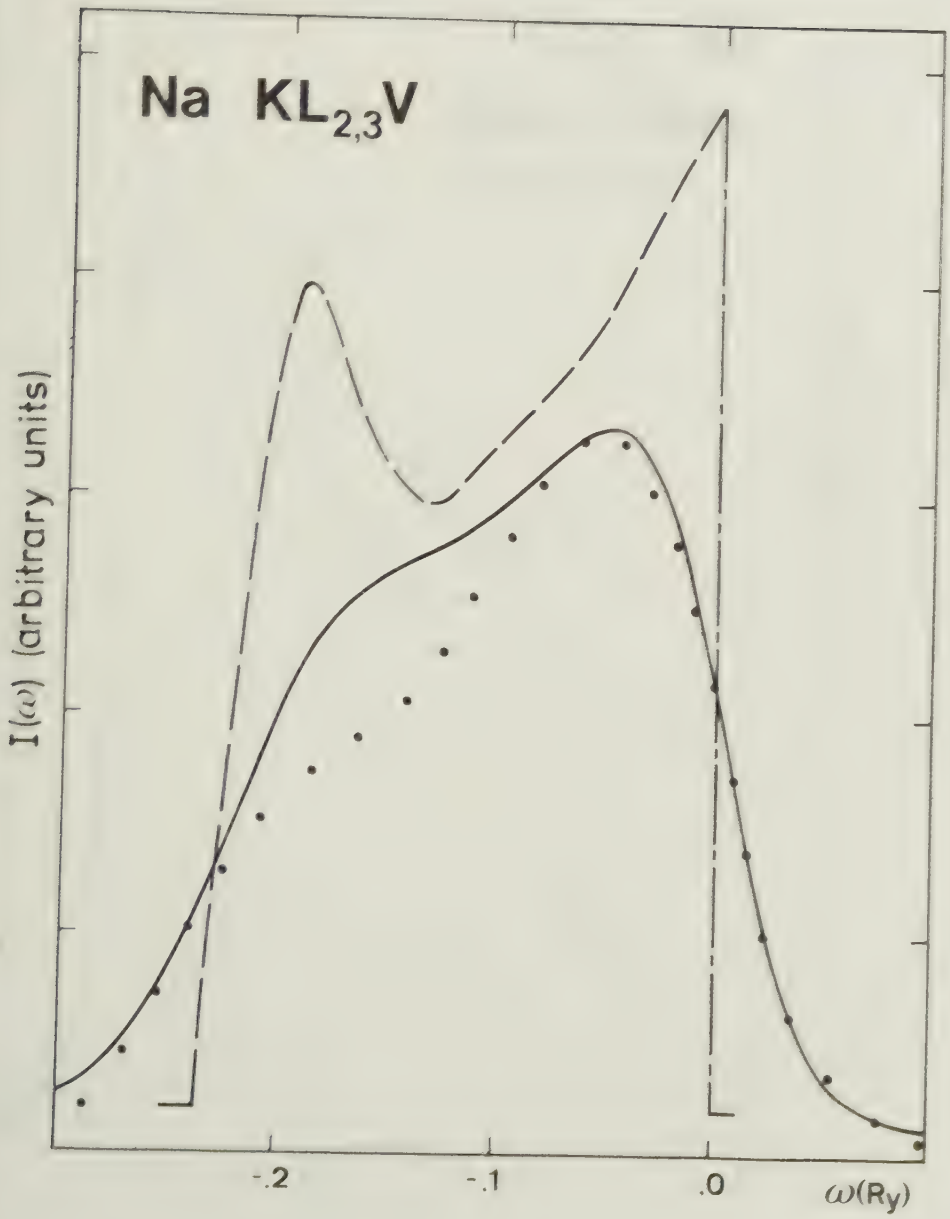


FIGURE 6

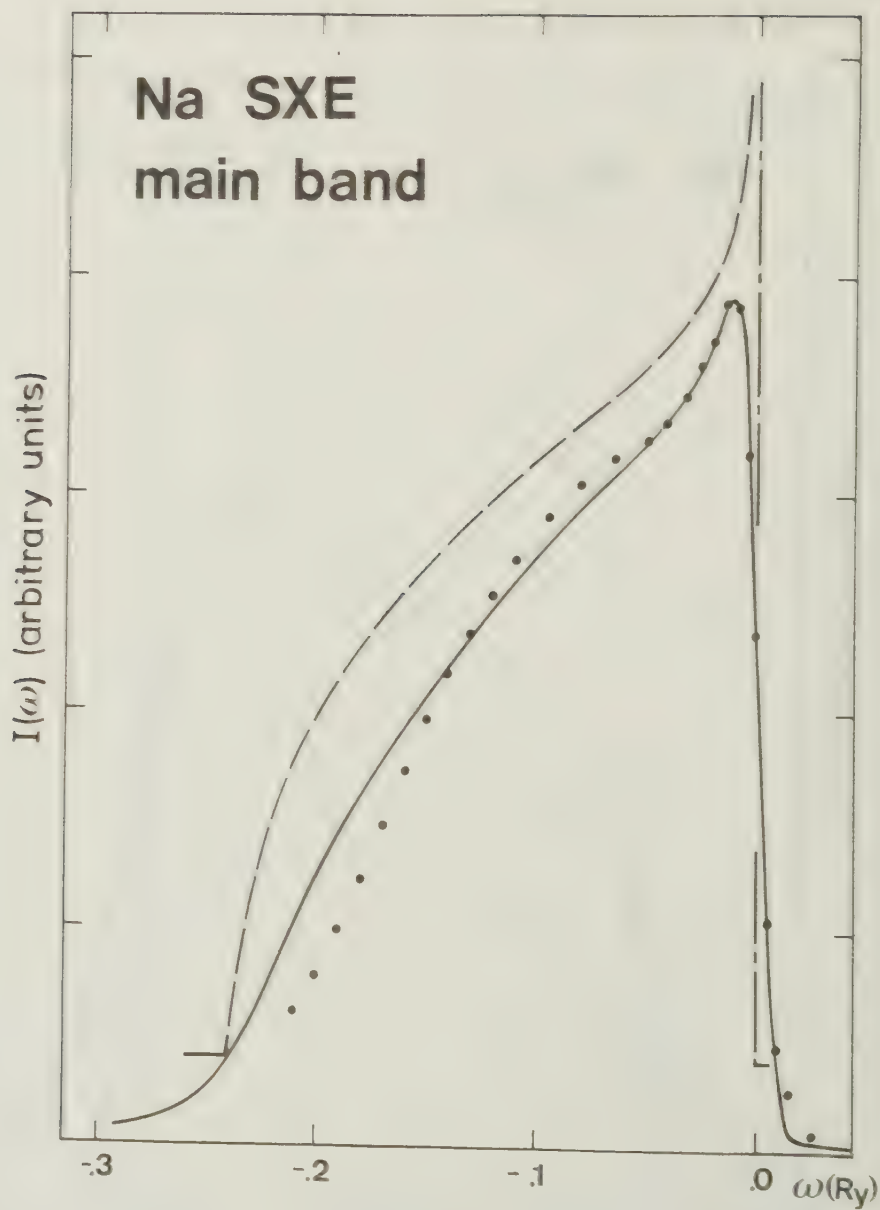
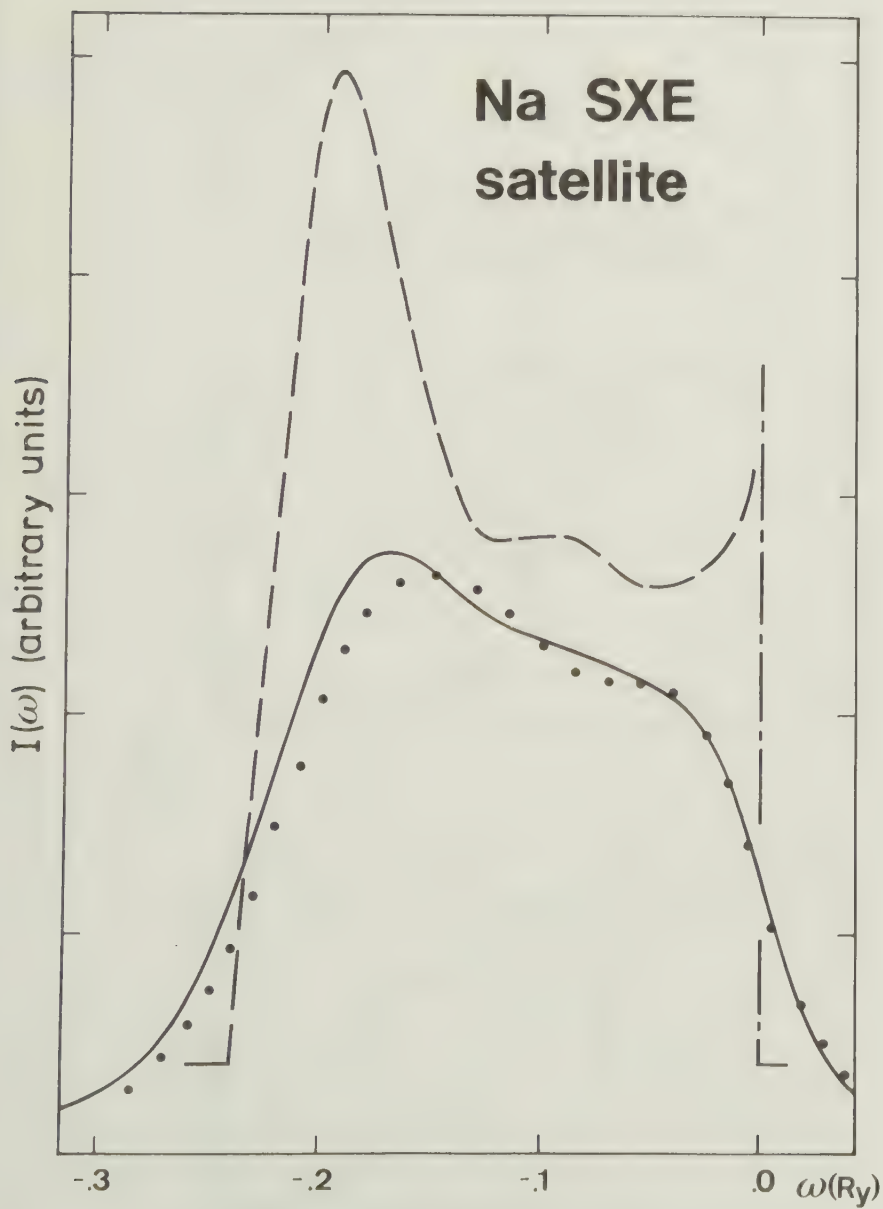


FIGURE 7



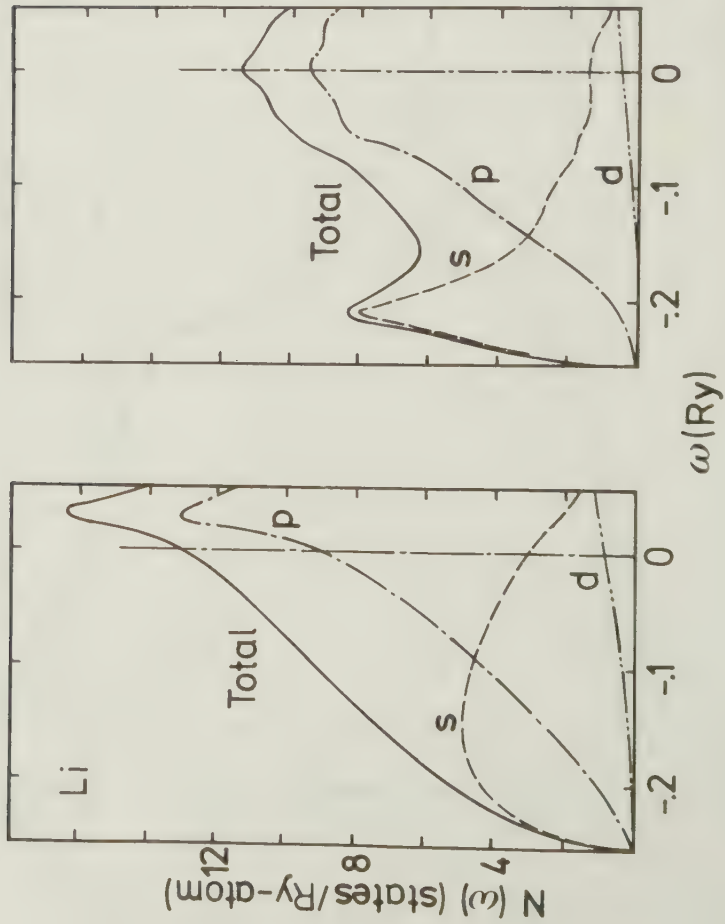


FIGURE 8

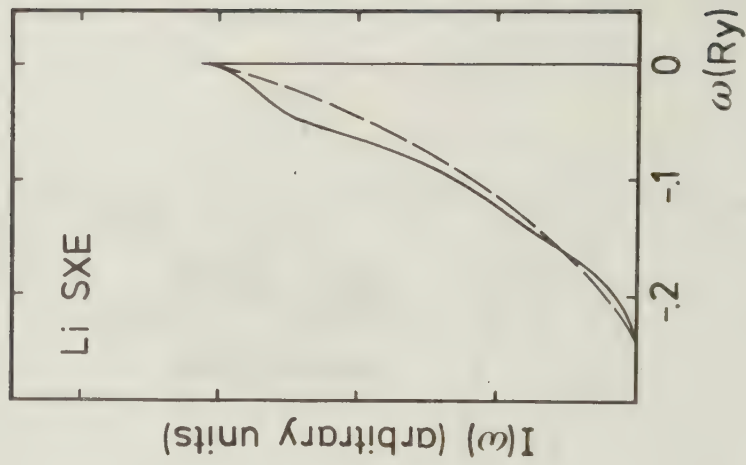


FIGURE 9

